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INVESTIGATION OF THE TECHNIQUE AND MATERIALS USED  
FOR MORDANT GILDING ON BYZANTINE AND POST-BYZANTINE  
ICONS AND WALL PAINTINGS

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A thesis submitted  
for the degree of Master of Philosophy  
University of Northumbria at Newcastle

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# **Abstract**

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The present study provides an account of the technique of mordant gilding and the materials used for the preparation of oil-mordants in Byzantine icon and mural painting.

Firstly, a brief history of Byzantium and of Byzantine art as developed from the foundation of the Empire in 330 A.D. to the present day is presented. The religious and symbolic character of Byzantine iconography and the history and technology of icons and wall paintings are then outlined. The techniques of water and mordant gilding as applied to both the Western and the Byzantine panel and mural painting are also explained, including a literature review of the documentary sources and the published works on oil-mordants used for gilding on panels and murals. A brief introduction on the nature of drying oils, the mechanisms of drying and ageing and the effects of heat bodying and dryers on their properties is also presented. Finally, the results of experiments conducted on linseed oil for the purpose of this study and the analysis carried out on samples taken from original paintings to confirm the use of oil-mordants in Byzantine painting are discussed.

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**BYZANTINE WORLD**

## A. Byzantine History

In order to introduce the reader to the world of Byzantine icons and wall paintings, it is essential to dedicate this first chapter to the presentation of an outline of Byzantine history and art. Before embarking on that, however, it was thought necessary to define the meaning of the words “Byzantine” and “Post-Byzantine”, as these terms will be continuously employed throughout the present study.

Byzantium was an ancient Greek city founded by the Megarian *Byzas* in the triangle of land formed at the junction of the Golden Horn, the Bosphorus and the sea of Marmara about 660 B.C. <sup>1</sup> In 324 A.D. the Roman Emperor *Constantine the Great* chose the same site to found a new city, which would become the cultural and administrative centre of the Roman Empire in the East, as well as his residence. <sup>2</sup> On 11<sup>th</sup> May 330 A.D. he formally inaugurated his city, which was named after him and was destined to become the capital of a new Empire: the “*New Rome*” that Constantine himself intended Constantinople to be. <sup>3</sup> Nevertheless, the old name of Byzantium was retained to describe the new state, designated by the general term “Byzantine”. This term has also been systematically employed in relation to the history, the culture and the art of Eastern Christendom.

Therefore, Byzantium was only the name of the old city on which Constantinople was built. However, this does not indicate what the actual Byzantine civilisation was built on. It is the combination of three fundamental elements that will lead to the comprehension of the conditions under which this new civilisation was born and evolved: Greek culture, the Roman Empire and the Christian East. Constantinople was constructed on an ancient Greek settlement and in a Greek-speaking territory; but it was a Roman city too, as a large

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<sup>1</sup> *Collins Dictionary of the English Language*, 2<sup>nd</sup> Edition, Collins (1986), p. 217.

<sup>2</sup> DURAND, J., *Byzantine Art*, Terrail, Paris (1999), p. 8.

<sup>3</sup> *Ibidem*, p. 8 & 14.

proportion of its inhabitants were Latin-speaking and “*New Rome which is Constantinople*” remained its official title to the end. Moreover, it was to be a Christian city and Christianity was an Oriental religion, based on the mysticism of the East and on Semitic conceptions.<sup>4, 5, 6</sup> Therefore, the history of Byzantium can be characterised as “*the history of the infiltration of Oriental ideas to tinge the Greco-Roman traditions*”.<sup>7</sup> “*Roman political concepts, Greek culture and the Christian faith were the main elements which determined Byzantine development. Without all three the Byzantine way of life would have been inconceivable. It was the integration of Hellenistic culture and the Christian religion within the Roman imperial framework that gave rise to the historical phenomenon which we know as the Byzantine Empire*”.<sup>8</sup>

The Byzantine Empire flourished for eleven centuries twenty-three years and eighteen days, until the 29<sup>th</sup> May 1453 A.D., the date on which the Turks conquered Constantinople. The Byzantine tradition, however, persisted even when Byzantium succumbed politically to the Ottoman Empire. Through a number of revivals it continued to develop and still survives today in the art of the Eastern Orthodox Church in Greece and to a great extent in the Balkan countries, which are the more direct inheritors of Byzantine culture. The term “Post- Byzantine” is in general use to determine the period from the fall of Constantinople to the present day<sup>9</sup> and characterises an artistic and religious period of Eastern Orthodoxy, rather than a historical one<sup>10</sup>. In the present study and primarily in relation to art, the term “Byzantine” is used to describe

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<sup>4</sup> Ibidem, p. 14.

<sup>5</sup> OSTROGORSKY, G., *History of the Byzantine State*, translated by J. Hussey, 2<sup>nd</sup> Edition, Oxford (1968), p. 27-29.

<sup>6</sup> TREADGOLD, W.T., *A History of the Byzantine State and Society*, Stanford University Press, California (1997), p. 119-136.

<sup>7</sup> RUNCIMAN, S., *Byzantine Civilization* (A reissue), University Paperbacks, Methuen, London (1961), p. 28.

<sup>8</sup> OSTROGORSKY, G., *History of the Byzantine State*, translated by J. Hussey, 2<sup>nd</sup> Edition, Oxford (1968), p. 27.

<sup>9</sup> DURAND, J., *Byzantine Art*, Terrail, Paris (1999), p. 10.

<sup>10</sup> CORMACK, R., *Byzantine Art*, Oxford University Press, Oxford (2000), p. 5.

the tradition and the culture that have been passed down over the centuries and not the specific historical period of Byzantium.

With both terms defined, it is now possible to pass onto a summary of the history of the Byzantine Empire, as presented by Runciman, <sup>11</sup> Ostrogorsky <sup>12</sup> and Treadgold <sup>13</sup> in their books on the Byzantine history. Constantine attained the imperial dignity in 306 A.D. and became the first Christian Emperor, a fact traditionally associated with the defeat of *Maxentius* at the battle of the Milvian Bridge in 312 A.D. In 330 A.D. he transferred the seat of the Roman Empire from Rome to Constantinople, adopted Christianity as the official state religion and at the end of the same century he recognised it as the one and only true faith. He died in 337 A.D. and a series of dynasties succeeded him to the imperial throne. In the first three centuries the dynasties were quite short, reaching only the third generation. During the last eight centuries, however, Byzantium was predominantly ruled by five large families: the Heraclians, the Isaurians, the Macedonians, the Comneni and the Palaeologi.

The fourth century is considered by many historians to be the passage from the Roman past to the Byzantine future and it may well be designated as *late Roman* or *early Byzantine*. <sup>14</sup> The Emperor *Theodosius the Great* (379-395 A.D.) was one of the most important personalities of this century. A new era began for the now Orthodox Empire and Theodosius was to be the last Emperor who would reign from Britain to the Euphrates. After his death the East and the West were definitively separated. The fifth century was marked by a series of successive Barbarian invasions, which led to the downfall of the

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<sup>11</sup> RUNCIMAN, S., *Byzantine Civilization* (A reissue), University Paperbacks, Methuen, London (1961).

<sup>12</sup> OSTROGORSKY, G., *History of the Byzantine State*, translated by J. Hussey, 2<sup>nd</sup> Edition, Oxford (1968).

<sup>13</sup> TREADGOLD, W.T., *A History of the Byzantine State and Society*, Stanford University Press, California (1997).

<sup>14</sup> See OSTROGORSKY, G., *History of the Byzantine State*, translated by J. Hussey, 2<sup>nd</sup> Edition, Oxford (1968), p. 29.

Western Empire. Under the reign of *Zeno* (474-491 A.D.) the first signs of separation between the Roman and the Byzantine Church began to become evident, while the Bulgars made their first appearance in the Balkans. Theologically, this first period of Byzantine history was marked by the Monophysite controversy and characterised by the crystallisation of the Eastern Christian thought through the Ecumenical Councils.

The second most prominent period in the Byzantine history opens in 518 A.D. with the accession of *Justin I*, who also initiated a new dynasty of Emperors. However, most Byzantinists acknowledge *Justinian* (527-565 A.D.) as the dominant figure of the sixth century. It was in his age that Byzantium became in all senses a flourishing, prosperous Empire. He managed to recover the territories of the old Imperial Rome and to expand its boundaries with new conquests. After having revised the already existing Roman Law codes, he issued his great Code in 529 A.D., one of the world's most famous legal systems. In addition, he was a great builder and it was under his reign that Saint Sophia, the Church of the Holy Wisdom and one of architecture's most great creations, was erected.<sup>15</sup> The age of Justinian is regarded to be the culmination of Early Christian art,<sup>16</sup> as well as the link between the Early Christian period and the main Byzantine era.

In the few decades following Justinian's death, his successors made some effort to continue his work, but it proved to be a hard task. During the seventh century, when the Heraclian dynasty was on the throne (610-711 A.D.), the Empire fell into chaos. The occupation of the Balkan peninsula by the Avars and the Slavs was followed by the Persian invasion in the eastern provinces. Then the Avaro-Persian siege of Constantinople, the rise of Islam and the Islamic conquest of Palestine, Syria, Egypt and the entire North African coast took place. Whilst facing

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<sup>15</sup> See TREADGOLD, W.T., *A History of the Byzantine State and Society*, Stanford University Press, California (1997), p. 207-217.

<sup>16</sup> TALBOT RICE, D., *Art of the Byzantine Era*, Thames & Hudson Ltd, London (1963), p. 47.

constant wars, Byzantium struggled to survive through the most eventful and dark years in Byzantine history.<sup>17</sup>

Throughout the eighth and the first half of the ninth century, which coincide historically with the reign of the Isaurian and the Amorian dynasties, the Empire encountered the Iconoclastic (i.e. image-breaking) controversy (726-843 A.D.). In 726 A.D. *Leo III* published a decree, which would not permit any worship of images or representations of the divine in religious art. A mass destruction of icons depicting Christ, the Virgin and saints followed and any new-built church had to be decorated with neutral, aniconic subjects. According to many scholars, iconoclasm was a political, anticlerical movement, rather than a theological one and its origin has also been ascribed to Islamic and Semitic influence.<sup>18</sup> Other important events that should be mentioned in this context are the adoption of Christianity as the official Bulgar religion by the king *Boris* in 864 A.D., as well as *Vladimir* prince of Kiev's Orthodox baptism in 988 A.D.<sup>19</sup> Vladimir's recognition of Christianity as the state religion was of extreme importance for Russia, who appropriated the Byzantine tradition and remained one of its most faithful successors to the present day.

The period from the end of Iconoclasm in 843 A.D. to the Latin conquest of Constantinople in 1204 A.D. is generally known as *Middle Byzantine* and regarded as the *Second Golden Age* in Byzantine history.<sup>20</sup> Two main dynasties reigned during this period, the Macedonian (867-1056 A.D) and the Comneni (1081-1185 A.D.).

Under the rule of the Macedonian house the Empire reached the climax of prosperity. The finest and most luxurious materials were used to decorate the palaces and churches. The artistic activity, after the

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<sup>17</sup> OSTROGORSKY, G., *History of the Byzantine State*, translated by J. Hussey, 2<sup>nd</sup> Edition, Oxford (1968), p. 87-146.

<sup>18</sup> See DURAND, J., *Byzantine Art*, Terrail, Paris (1999), p. 68-71.

<sup>19</sup> Although this event occurred in the next distinct historical period, it is stated in this context due to its strong connection with the precedent era.

<sup>20</sup> DURAND, J., *Byzantine Art*, Terrail, Paris (1999), p. 80-86.

reestablishment of icon worship, was mainly characterised by a spirit of innovation, designed to restore Byzantium's old glory. Hence the characterisation of the tenth century as *Macedonian Renaissance*,<sup>21</sup> a term that addresses not only the artistic renovation, but also the expansion of the imperial boundaries. With this Byzantium once again became the dominating force in the Eastern Mediterranean. Basil II (976-1025 A.D.), nicknamed *Basil the Bulgaroctonus* (Bulgar-slayer) because of his victories over the Bulgars, is regarded as one of the most important Emperors of the dynasty.<sup>22</sup> After his death the Empire suffered new reverses, due to the arrival of a new power from Central Asia, the Seljuk Turks. The final separation of the churches of Constantinople and Rome was probably the most significant event that took place at the end of the Macedonian age, in 1054 A.D. This schism led to the division of Christendom into two faiths, the Orthodox and the Roman Catholic, a situation that has remained unchanged to date.

Under the Comneni a new menace, known as the Crusades, emerged from the West. Relations between East and West became closer and expeditions in the form of large groups of pilgrims started travelling to the East. It is believed that the Crusaders were stimulated by religion but led by politicians who coveted Constantinople and its position at the crossing of two of the greatest trade routes.<sup>23</sup> Thus, after four successive Crusades spanning a period of more than hundred years, Constantinople was occupied and sacked by the Crusaders in 1204 A.D. A Latin dynasty was set up to rule the city and the Empire was fragmented. Salonica became the second Latin kingdom, the Venetians established themselves in the Aegean islands and Crete, while the mainland was divided in three minor independent principalities: the Empire of Nicea, the Despotate of Epirus and the Empire of Trebizond. Of these three small empires, only that of Nicea managed to recover its

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<sup>21</sup> CORMACK, R., *Byzantine Art*, Oxford University Press, Oxford (2000), p. 129-142.

<sup>22</sup> OSTROGORSKY, G., *History of the Byzantine State*, translated by J. Hussey, 2<sup>nd</sup> Edition, Oxford (1968), p. 298-315.

<sup>23</sup> Ibidem, p. 361.



power and to gradually win back Macedonia and Salonica. In 1259 A.D. *Michael Palaeologos* came to the throne and after allying with the Genoese against the Venetians, who were responsible for the Fourth Crusade, he captured back Constantinople in 1261 A.D.

During the Palaeologue dynasty (1261-1453 A.D.) the capital fell into a state of impoverishment, mostly due to its sack by the Latins and the gradual shrinking of the imperial territories.<sup>24</sup> In the thirteenth century a young Turkish tribe that was brought from Asia, the Ottoman Turks, settled at the eastern borders of the Empire and was organised into a military power. By the middle of the fourteenth century they began to gradually advance towards Europe and in 1422 A.D. they laid siege to Constantinople. The final day came in 1453 A.D. On 29<sup>th</sup> May, after seven weeks of defence, Constantinople fell into Muslim hands. This marked the end of the Byzantine Empire. A table of the most significant events of the Byzantine history is shown in the Appendix, Figure 1.

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<sup>24</sup> Ibidem, chapter VIII, p. 466-572.

## B. Byzantine Art

With the framework of Byzantine history established, it is now possible to briefly present a sketch of Byzantine art by first tracing its origins back to the inception of the Byzantine Empire. The main source of reference is Talbot Rice and summarised below is the information given in his books on Byzantine art.<sup>25, 26</sup> Special attention will be given to icons and wall paintings, as they are the prime subject of this study. Byzantine art is a valuable legacy Byzantium left to the world, testimony of the advancement that this civilisation reached during its eleven centuries. In order to fully understand the character of this art and its evolution through time, the origins of Byzantine culture should be more thoroughly traced. Byzantinists believe that the main sources of influence upon Byzantium derived from both Eastern and Western civilisations, which were either developing or already existed when the Empire was founded. Talbot Rice classifies these civilisations into seven principal groups, according to the regions in which they flourished: Greece and the Hellenistic world, Asia Minor, Rome and Italy, Syria and the Semitic East, northern Mesopotamia, southern Persia (Iran) and lower Mesopotamia (Iraq), and northern Persia (Altai-Iran).<sup>27</sup>

As already mentioned in the first part of this chapter, the Hellenic tradition played a fundamental role in the formation of the Byzantine character. Not only was Constantinople founded on Greek land, but Byzantium also incorporated all the Greek territories, as well as all the large cities of the Mediterranean coastlands, i.e. Alexandria, Antioch, Miletus, Priene, Ephesus and Pergamon. Although these cities formed part of the Roman Empire from around the end of the third century

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<sup>25</sup> TALBOT RICE, D., *Byzantine Art*, Oxford University Press, Oxford (1935).

<sup>26</sup> TALBOT RICE, D., *Art of the Byzantine Era*, Thames & Hudson Ltd, London (1963).

<sup>27</sup> TALBOT RICE, D., *Byzantine Art*, Oxford University Press, Oxford (1935), p. 29.

B.C., the Hellenic culture remained vivid and was thus conveyed to Byzantium.<sup>28</sup>

Roman art was based to a great extent on the idealistic forms of Greek art. Nevertheless, by the first Christian years and under the influence of local factors it had already crystallised into its own individual form. When Constantine transferred the centre of the Empire to the East (330 A.D.), together with the court and the government, the imperial art was also brought from Rome to the new capital. Consequently, it is believed to have played an important role in the development of art during the first two centuries of the new-founded state.<sup>29</sup>

Talbot Rice and other historians agree that a further significant influence upon the evolution of Byzantine art came from the Semitic East. The Semitic tendency in art, which developed in the extended area of Syria, opposed the Hellenic one. In Semitic art the interest is not in the appearance or the external beauty of the figures and objects, but in revealing their essence and their inner meaning.<sup>30</sup> Its influence became apparent in Byzantine art when the figures adopted the frontal pose and were enlarged to underline their importance. Overall, it seems to be the infiltration of an elaborated Semitic art into the Hellenic culture that led to the creation of this particular, unique style that is recognisably Byzantine.

Yet, according to Talbot Rice, Byzantine art was also the result of a blend of various other elements, which originated from other Eastern cultures that germinated before or during the formation of Byzantium. The areas of Mesopotamia and Persia were the home of a number of very important civilisations, with a far-reaching effect on the evolution but not on the creation of Byzantine culture. In earlier times the Semitic-

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<sup>28</sup> See also TREADGOLD, W.T., *A History of the Byzantine State and Society*, Stanford University Press, California (1997), p. 3-5.

<sup>29</sup> See also DURAND, J., *Byzantine Art*, Terrail, Paris (1999), p. 16.

<sup>30</sup> TALBOT RICE, D., *Art of the Byzantine Era*, Thames & Hudson Ltd, London (1963), p. 34-37.

based Assyrian civilisation thrived in northern Mesopotamia, while at the beginning of the Christian age the strongly orientalised Parthian civilisation was born in the Tigris basin. In the third century the Sasanian dynasty was established in southern Mesopotamia and southern Persia and a new art, known as Sasanian, arose.<sup>31</sup> There are also other types of formalistic and non-representational art that originated in Central Asia and in Altai-Iran and to which some influence on Byzantine art can be attributed. These include the Anatolian and the Scythian, but the presentation of the various existing theories on these types of art and their relation with Byzantium is not the scope of this study.<sup>32</sup> It should, however, be borne in mind that the entire geographical area had been affected by the Hellenistic culture that *Alexander the Great* established in the East, which again highlights the importance of the Hellenic influence upon Byzantium.<sup>33</sup>

Nevertheless, there are also other equally important factors responsible for the character that Byzantine art, as expression of the Byzantine culture, assumed over the years, with religion being one of them.<sup>34</sup> Until the age of Justinian, Byzantium bore imperial features that had been inherited from the Roman Empire. Under Justinian (527-565 A.D.), however, Christianity triumphed and religion began to dictate the form and limitations of people's lives. Therefore, the whole civilisation and in particular art acquired a religious character.<sup>35</sup> The most magnificent buildings were churches and the most glorious works of art were religious, all were created to serve the faith. At the same time, art was used to magnify the Emperor and to assert his deification, leading to the consequent glorification of the State and of God.<sup>36</sup>

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<sup>31</sup> Later this was to become an essential element in Muslim art.

<sup>32</sup> For a more analytical review see TALBOT RICE, D., *Byzantine Art*, Oxford University Press, Oxford (1935), p. 35-40.

<sup>33</sup> See note 28.

<sup>34</sup> CORMACK, R., *Byzantine Art*, Oxford University Press, Oxford (2000), p. 2-3.

<sup>35</sup> TALBOT RICE, D., *Art of the Byzantine Era*, Thames & Hudson Ltd, London (1963), p. 47-62.

<sup>36</sup> CORMACK, R., *Byzantine Art*, Oxford University Press, Oxford (2000), p. 37-62.

The forms with which Byzantine art chose to express its ideals were various: architecture, painting, mosaic, sculpture, manuscript illumination, enamels, textiles, ivories, jewellery and metalwork. Although each of these mediums produced unique pieces of work, Byzantine art was brought to its greatest heights by icon painting and mural decoration. A brief outline of their evolution through the centuries of Byzantine history follows, as presented by Talbot Rice,<sup>37, 38</sup> Durand<sup>39</sup> and Cormack<sup>40</sup> in their books on Byzantine art.

In Constantine's day (324-337 A.D.) pictorial art was still in its infancy. Simple, symbolic catacomb painting was adopted from Greco-Roman art, with neutral decoration and scenes, like that of "*The Good Shepherd*", prevailing.<sup>41</sup> During Justinian's reign (527-565 A.D.), an amazing number of churches and monasteries were erected in various parts of the Empire and the need for interior decoration intensified for the first time.<sup>42</sup> Moreover, it is precisely in this period that the saint's portrait i.e. the icon, started to become popular and its cult assumed great importance in Christian devotion.<sup>43</sup> Very few works of art from the seventh to the tenth centuries have survived, partly because of the Muslim invasions, but mostly because of their destruction by the iconoclasts (726-843 A.D.).<sup>44</sup>

With the reestablishment of icons in worship, vigorous artistic activity was initiated in Byzantium, as the task of the redecoration of the churches remerged.<sup>45</sup> Mosaic decoration gradually began to be replaced by the cheaper technique of mural painting and a new iconography began to evolve. During the period of the Crusades,

<sup>37</sup> TALBOT RICE, D., *Byzantine Art*, Oxford University Press, Oxford (1935).

<sup>38</sup> TALBOT RICE, D., *Art of the Byzantine Era*, Thames & Hudson Ltd, London (1963).

<sup>39</sup> DURAND, J., *Byzantine Art*, Terrail, Paris (1999).

<sup>40</sup> CORMACK, R., *Byzantine Art*, Oxford University Press, Oxford (2000).

<sup>41</sup> Ibidem, p. 12-15.

<sup>42</sup> Ibidem, p. 37-62.

<sup>43</sup> Ibidem, p. 66.

<sup>44</sup> See note 18.

<sup>45</sup> DURAND, J., *Byzantine Art*, Terrail, Paris (1999), p. 97-108.

Byzantine art accepted influences from both the West and the East.<sup>46</sup> It is also in this period that the painters' individual personality started to become apparent through their work and anonymity was progressively eliminated.<sup>47</sup> With the Latin conquest of Constantinople (1204 A.D.) the economy of the Empire was seriously affected.<sup>48</sup> Wall paintings were used as substitutes for mosaics in the main decoration of the churches and some of the finest works of art of this kind were produced in this period. At the end of the Palaeologue age (1453 A.D.) new distinctive iconographic styles arose and several schools developed.<sup>49</sup> Thus the principal era of Byzantine art was brought to an end and the Post-Byzantine period had just begun.

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<sup>46</sup> CORMACK, R., *Byzantine Art*, Oxford University Press, Oxford (2000), p. 187-200.

<sup>47</sup> Ibidem, p. 197.

<sup>48</sup> DURAND, J., *Byzantine Art*, Terrail, Paris (1999), p. 164-168.

<sup>49</sup> Ibidem, p. 178-196.

## **ICONS AND WALL PAINTINGS**

## A. Introduction to Byzantine Iconography

Before closer examination of the use and technology of Byzantine and Post-Byzantine icons and wall paintings, it is important to first draw attention to the essence of Byzantine religious painting or rather iconography.<sup>1</sup> As already indicated, Byzantine art, and in particular Byzantine iconography, is characterised by a formalistic style, which does not seek to reproduce nature or to portray people and objects realistically but aims, by means of line and form, to convey its own deeper messages.<sup>2</sup> Moore notes that according to the Eastern Orthodox doctrine established after the official recognition of the use and veneration of images, religious paintings in general are “*sacred manifestations pointing beyond themselves to the eternal archetype who is unseen in heaven*”.<sup>3</sup> Therefore, they cannot be naturalistic for they would only appeal to the spectator and generate emotion and admiration, without enabling him to discover and reflect upon the ideas that lie beneath. Rather than representations of scenes, they must be seen as windows that introduce the faithful into a mystical world and play the role of the mediator between the mortal and the divine.<sup>4</sup>

The programme of Byzantine iconography comprises a very wide range of figures and scenes, whose number gradually increased in the course of the long history of the Eastern Orthodox Church. The Apostles, the Evangelists and the Church Fathers who contributed to the establishment and spread of Christianity have been repeatedly represented alongside various saints, martyrs and heroes of the faith, whose sanctity had been acknowledged by the Orthodox Church.

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<sup>1</sup> During recent centuries the Greek term “hagiography”, deriving from the word “*ἅγιος*” i.e. saint, has also been employed to denote the art of depicting saints.

<sup>2</sup> See chapter 1, p. 14.

<sup>3</sup> MOORE, A.C., *Iconography of Religions. An Introduction*, Fortress Press, Philadelphia (1977), p. 247.

<sup>4</sup> CORMACK, R., *Byzantine Art*, Oxford University Press, Oxford (2000), p. 217.



Scenes of the most significant events in the life of Christ, the Virgin and the saints, together with other stories from the Bible, constitute another vast iconographic field. A large number of different versions and manners of depicting the same scene, owing to the various traditions, influences and schools that were developed during the long-lasting history of Byzantine art, should be added to the above. <sup>5</sup>

Byzantine iconography, in order to lead the believer into the inner meaning of a representation, combines the pictorial features with another very powerful tool: symbolism. Sendler, <sup>6</sup> James, <sup>7</sup> and Chryssoulakis *et al.* <sup>8</sup> present an overview of the role of symbolism in Byzantine iconography.

Light is one of the most meaningful symbols used in Byzantine iconography. The natural light and the shadows that give shape to the objects are completely eliminated here. The religious image is overwhelmed by a supernatural light, which springs from the figures and the objects themselves and reflects an internal power. <sup>9</sup>

Colour is another element that has assumed symbolic meaning in Byzantine iconography. Red is a lively colour, signifying energy and vigour, the passionate love and burning zeal for the faith, the royal glory; it is also a reminder of blood, used therefore to symbolise martyrdom or even sin and it is directly associated with the Holy Spirit. Yellow expresses the temperance of humility, the absence of egoism and self-projection. White has always been considered as the symbol of innocence and purity, as well as holiness, wisdom and spiritual depth. Black represents chaos and death, the denial of light, and symbolises

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<sup>5</sup> Ibidem, p. 210-211.

<sup>6</sup> SENDLER, E., *The Icon: Image of the Invisible*, translated by Fr. S. Bigham, Oakwood Publications (1988), Section II.

<sup>7</sup> JAMES, L., *Light and Colour in Byzantine Art*, Clarendon Press, Oxford (1996).

<sup>8</sup> CHRYSSOULAKIS, Y., SISTER DANIILIA, *The Contribution of Modern Technologies to the True Interpretation of the Inner Spiritual Meaning Expressed through Byzantine Iconography*, ORMYLIA Art Diagnosis Centre, Ormylia (2000).

<sup>9</sup> SENDLER, E., *The Icon: Image of the Invisible*, translated by Fr. S. Bigham, Oakwood Publications (1988), p. 173-179.

cleansing, receptivity and purification. Green is the colour that prevails in nature during springtime, when everything revives, and as such symbolises new life, tranquillity and hope; it is also closely associated with the Trinity. Blue is the colour of the sky and usually refers to heaven, but also represents eternity, profound discernment, mercifulness, fidelity and truth.<sup>10</sup>

However, symbolism is not limited to colours. Certain numbers, whose meaning cannot be decoded immediately, can also be encountered in Byzantine iconography. According to Hulme, the most commonly used numbers are two, for the two natures of Christ, the human and the divine, and three for the Trinity. Pythagoras called three the number of completion, representing the beginning, the middle and the end. Seven was regarded by old writers as the number of perfection. One of the numerous examples that can be quoted is the creation of the world, with the seventh day marking its completion. Twelve is the number of the Apostles and has been a favourite one in art symbolism, also used to represent the Church in a wider sense. Forty is the number that expresses a period of probation or trial, with the most characteristic example being the forty days of fasting of Christ in the wilderness.<sup>11</sup>

Other symbolic principles that introduce the believer to the meaning of the depicted scenes include the geometrical patterns, as well as the unusual use of perspective. Hence, the square represents the earth, the triangle the Trinity and the circle eternity and divine unity. The frequent use of inverse perspective that points outside the picture towards the spectator changes the significance of the third dimension and creates a sense of freedom, where there exist no laws of time, space or gravity.<sup>12</sup>

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<sup>10</sup> Ibidem, p. 153-161.

<sup>11</sup> HULME, F.E., *The History, Principles and Practice of Symbolism in Christian Art*, Swan Sonnenschein & Co. Lim., London (1908).

<sup>12</sup> For an overview on the theories on inversed perspective see SENDLER, E., *The Icon: Image of the Invisible*, translated by Fr. S. Bigham, Oakwood Publications (1988), p. 135-148.

Gold is an element that occupies a distinctive position and bears its own symbolism in Byzantine iconography. Its brightness and warmth evokes the sun and the light of heaven, whereas its main noble metal properties, such as its worth, purity, endurance and the incorruptibility refer the believer to the main features of a Christian life. It therefore represents for Christians eternal life, faith and above all Christ Himself: the Sun of justice, the Light of the world and the Splendour of the rising sun. A more elaborate study of the role of gold in Byzantine iconography can be found in the following chapter of this study.<sup>13, 14</sup>

It should, however, be noted that religious symbolism extends beyond painting. The church, the liturgy, the chanting and the lighting are symbolic and it is their interrelation that introduces the believer to the Orthodox worship and enables him to experience its deep mysticism.

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<sup>13</sup> CHRYSSOULAKIS, Y., SISTER DANIILIA, *The Contribution of Modern Technologies to the True Interpretation of the Inner Spiritual Meaning Expressed through Byzantine Iconography*, ORMYLIA Art Diagnosis Centre, Ormylia (2000), p. 13.

<sup>14</sup> SENDLER, E., *The Icon: Image of the Invisible*, translated by Fr. S. Bigham, Oakwood Publications (1988), p. 172-173.

## B. Icons: Function, Evolution and Technology

The term “icon” derives from the Greek word “εἰκών” i.e. image, and was originally used to describe first portraits of Byzantine Emperors and then any representations of religious subjects <sup>15</sup>: *“Thus the Byzantine icon may be defined as a representation of a sacred subject on a portable plaque of wood, stone or metal, no matter what the technique employed – painting on wood surfaced with plaster, enamel-work or mosaic”*. <sup>16</sup> Later on, however, the term was restricted to portable panel paintings.

The word was first encountered in the book of Genesis to define man as *“made in the icon of God”*. <sup>17</sup> According to the doctrine of incarnation, which supports theologically the use and veneration of icons, Jesus Christ is the first and perfect icon of God Himself; saints are the living icons of Christ; the Bible is His verbal icon; the Church is also an icon, which reflects heaven and the Kingdom of God, as was Byzantium. Therefore, it becomes clear that the reverence expressed in every part of the religious practice in the Eastern Church is meant to return to Christ, including the painted images i.e. the icons. <sup>18</sup>

Furthermore, icons are very closely related to Christian teaching, as they are its visual representations: *“For that which a written document is to those who can read, that a picture is to the unlettered who look at it. Even the unlearned see in that what course they ought to follow; even those who do not know the alphabet can read there”*. <sup>19</sup>

Icons are also linked with the life of the Church and constitute an integral part of the liturgy and of the circle of festivals during the Church year. Their main position inside the church is on the icon stand

<sup>15</sup> BAGGLEY, J., *Doors of Perception – Icons and Their Spiritual Significance*, St. Vladimir’s Seminar Press, N. York (1995), p. 1.

<sup>16</sup> GRABAR, A., *Byzantine Painting*, Skira (1953), p. 187.

<sup>17</sup> *Book of Genesis*, chapter 1, 27.

<sup>18</sup> For an overview on the theological elements of icons see SENDLER, E., *The Icon: Image of the Invisible*, translated by Fr. S. Bigham, Oakwood Publications (1988), p. 39-49.

<sup>19</sup> BEVAN, E., *Holy images*, Allen & Unwin (1940), p. 126.

or “*iconostasis*” a screen that separates the nave from the sanctuary and also symbolically separates earth from heaven. In a carefully planned scheme, the whole history of the life of the Church is displayed in the five tiers of the iconostasis. The Old Testament Patriarchs and Prophets are at the top, the most important events of the Virgin’s and Christ’s lives are directly below and the representations of the Apostles, the Evangelists, the Church Fathers, the saints and the Archangels are at the bottom. Devotional icons are placed on lecterns for the faithful to kiss, while on particular festivals processional icons are carried by the priests around the church.<sup>20, 21</sup> At the same time icons reveal to the believer the way to overcome the boundary between the two worlds, the human and the divine, and find redemption.<sup>22</sup>

The use of icons, however, has also become very popular in domestic devotion, because of their intimate character as well as their portability, which allows believers to transport them and keep them in their homes.<sup>23</sup> Their veneration is also closely connected with their miraculous powers of blessing and healing and they are often regarded as sources of divine protection. Therefore, most scholars agree that icons are primarily a means of communication between the faithful and the Kingdom of Heaven and one can go deeper into their essence, according to the level of spirituality that one uses as reference.

The first icon “*not made by hands*”<sup>24</sup> is traditionally considered to have been created when Christ was asked for a portrait and gave the imprint that came on a piece of fabric He dried His face with.<sup>25</sup> The

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<sup>20</sup> BAGGLEY, J., *Doors of Perception – Icons and Their Spiritual Significance*, St. Vladimir’s Seminar Press, N. York (1995), p. 91-95.

<sup>21</sup> CORMACK, R., *Byzantine Art*, Oxford University Press, Oxford (2000), p. 211.

<sup>22</sup> BAGGLEY, J., *Doors of Perception – Icons and Their Spiritual Significance*, St. Vladimir’s Seminar Press, N. York (1995), p. 4.

<sup>23</sup> Ibidem, p. 97.

<sup>24</sup> This type of icon is known as “*αχειροποίητος*” (acheiropoiitos).

<sup>25</sup> This representation is called “*Μανδήλιον*” (Mandylium) or “Holy Face” and has been the prototype of many later icons. See CORMACK, R., *Byzantine Art*, Oxford University Press, Oxford (2000), p. 136-137.

legend says that the Apostle Luke was the first to paint an icon, depicting the Mother of God holding the child Christ in her left arm and pointing towards Him with her right hand.<sup>26</sup> According to Byzantinists, however, the origin of the icon painting must be traced back to the Egyptians' funeral portraits that were used to cover the faces of mummies, known as "*Fayum portraits*".<sup>27</sup>

The few examples of the earliest icons in existence today belong to the late fifth and the sixth century and most of them are products of the Coptic (Egyptian Christian) art.<sup>28</sup> During the sixth and the seventh centuries icons became the object of growing worship. This is thought to be mainly due to the strong popular belief in their miraculous powers.<sup>29</sup> At the same time an increase was noticed in their manufacture and sale by independent, powerful monasteries. As already mentioned, the iconoclastic period (726-843 A.D.) was marked by the systematic removal and destruction of icons as well as a ban on their manufacture.<sup>30</sup> Nevertheless, small icons became quite popular as they could be easily hidden and it is likely that the practice of keeping icons at home originates from that period.

From the *Middle Byzantine* period or *Second Golden Age* only a handful of icons have survived.<sup>31</sup> It is, however, from around the twelfth century that icon painting began to obtain a dominant position in Byzantine art and icon manufacture developed throughout the whole of the Byzantine world.<sup>32</sup> Firm rules now govern iconography, while there is an increasing number of figures or even scenes that can be represented in a single icon. The close contacts between Byzantium and

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<sup>26</sup> This iconographic type is known as "*Οδηγήτρια*" (Hodigitria) or "Indicator of the Way". See CORMACK, R., *Byzantine Art*, Oxford University Press, Oxford (2000), p. 28-29.

<sup>27</sup> BAGGLEY, J., *Doors of Perception – Icons and Their Spiritual Significance*, St. Vladimir's Seminar Press, N. York (1995), p. 100-101.

<sup>28</sup> Ibidem, p. 101.

<sup>29</sup> DURAND, J., *Byzantine Art*, Terrail, Paris (1999), p. 71.

<sup>30</sup> See chapter 1, p. 10 & 16.

<sup>31</sup> DURAND, J., *Byzantine Art*, Terrail, Paris (1999), p. 127-131.

<sup>32</sup> CORMACK, R., *Byzantine Art*, Oxford University Press, Oxford (2000), p. 150-156.

the West, as a result of the Crusades, led to the development of the “*Crusader Art*”, which was characterised by some Western influence.<sup>33</sup> With the Latin conquest of Constantinople many painters fled the city to establish themselves in the minor empires and the Balkan countries and a phase of high artistic production began.<sup>34</sup>

In the fourteenth century two major iconographic styles predominated in Constantinople, Greece and the Balkans, that resulted in the creation of two different painting schools: the Macedonian and the Cretan.<sup>35</sup> When Byzantium drew to a close, the major cities such as Constantinople, Salonica (from quite early times the second city of the Empire) and Ochrid in the southern Slav area continued to be cultural and artistic centres. This study will only engage in the development of Post-Byzantine icon painting in the Greek world and therefore addresses the most immediate inheritor of the Byzantine style.

A brief description of the two distinct painting schools follows. During the fourteenth century the Empire was in crisis and many painters from Constantinople migrated to Crete, a Venetian colony that only fell to the Turks in the seventeenth century. Together with their Orthodox religion and Byzantine culture, those painters brought with them the pure Constantinopolitan style of icon painting, this resulted in the formation of a new school, known as the “*Cretan School*”. In the north of Greece, however, another school that was centred in Salonica had developed, later on named the “*Macedonian School*”. The main characteristics that distinguish the artistic production of the two schools can be briefly summarised in the bright colouring, the light touch, the rendering of the details and the rich iconographic system of the former, compared to the less sophisticated and more dramatic manner of the latter. Neither of the two streams, however, was limited to the geographic area in which

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<sup>33</sup> Ibidem, p. 188.

<sup>34</sup> DURAND, J., *Byzantine Art*, Terrail, Paris (1999), p. 178-180.

<sup>35</sup> These two terms were first applied by the French Byzantinist Gabriel Millet to determine the two distinctively different manners of icon and mural painting in Greece.

they were originally created and their influence spread outside the borders of the Greek territory. It should be noted in this context that the Macedonian school is more closely related to the art of mural painting, whereas the Cretan is better expressed in icons, because of the freedom of a wider palette and the possibility of rendering the detail, characteristic of icon painting.<sup>36, 37</sup>

Quite distinct from it is the so-called “*Greek-Italian School*”. This was developed from painters that had largely worked in regions under Italian domination, such as the western Greek islands and Crete, or even Italy itself. The style of this school remains Byzantine in essence with the introduction of a few western elements.<sup>38</sup> Workshops in other Greek provinces, such as Smyrna or Pontus developed a wholly provincial style, which was occasionally characteristic of the general area in which they operated. In big monastic communities, however, like those of Mount Athos and Meteora that were hardly disturbed by the conquerors, distinct local schools flourished, e.g. the Athonite school of the sixteenth and seventeenth centuries.<sup>39</sup>

Most Byzantinists agree that two main techniques were developed in the art of icon painting, differentiated according to the binding medium used for the tempering of the pigments.<sup>40</sup> In the first technique, known as “*encaustic*”, the medium was wax that was mixed with the various pigments while still warm and then applied by means of a hot metal tool. The very few examples of encaustic icons that have survived belong to the early Christian centuries and are characteristic of Coptic art.<sup>41</sup> The other technique that was adopted by Byzantines and later became

<sup>36</sup> TALBOT RICE, D., *Art of the Byzantine Era*, Thames & Hudson Ltd, London (1963), p. 219-264.

<sup>37</sup> DRANDAKI, A., *Greek Icons*, translated by J. Avgherinos, Skira (2002), p. 4-6.

<sup>38</sup> TALBOT RICE, D., *Art of the Byzantine Era*, Thames & Hudson Ltd, London (1963), p. 243.

<sup>39</sup> Ibidem, p. 262.

<sup>40</sup> See CORMACK, R., *Byzantine Art*, Oxford University Press, Oxford (2000), p. 69 & 111.

<sup>41</sup> DURAND, J., *Byzantine Art*, Terrail, Paris (1999), p. 40-43.



the traditional icon painting technique is “*egg tempera*”. In this case the binding medium was egg yolk diluted with water to which a couple of drops of vinegar were added for the purpose of balancing the greasiness of the yolk, preserving the mixture and making it easier to use.<sup>42</sup>

Certain technical aspects of the icon painting have been presented by Sendler<sup>43</sup> and Baggley<sup>44</sup> in their monographs. The main stages are summarized in the following pages. The substrate on which icons were painted was wood, although other materials have also been occasionally used, for example stone. Wood has certain properties that make it an adequate carrier for painting and others that operate as disadvantages. It can be easily cut and shaped into a flat board, it is quite strong and therefore resistant to impact, but the fact that it is hygroscopic makes it susceptible to variations of temperature and humidity. The wood chosen to support an icon was preferably non-resinous. The more frequently used were sycamore, poplar, cypress, oak, birch, beech, alder and lime. The selected tangentially sawn plank or preferably the quarter-sawn (radial) plank cut across the diameter of the tree trunk, had then to be carefully seasoned for a number of years. The final board or boards glued together to form a panel were strengthened by battens fixed to their back perpendicular to the direction of the grain to avoid warping. In most cases raised borders were created to serve as a frame, while the recessed space constituted the main painting surface. Alternatively, the effect of a frame could be achieved by a painted margin.

The prepared panel had then to be planed and polished to an even surface, ready to accept the gesso ground. The gesso mixture, which was made with gypsum (calcium sulphate often burnt to anhydrite) and animal glue, was applied on the wooden carrier in several coats in order to form a thick and smooth surface upon which the painting and gilding

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<sup>42</sup> Ibidem, p. 128.

<sup>43</sup> SENDLER, E., *The Icon: Image of the Invisible*, translated by Fr. S. Bigham, Oakwood Publications (1988), Section III, p. 185-238.

<sup>44</sup> BAGGLEY, J., *Doors of Perception - Icons and Their Spiritual Significance*, St. Vladimir's Seminar Press, N. York (1995), p. 99-105.

would be performed.<sup>45</sup> Usually one or two coats of glue size were applied first to reduce the absorbency of the wood and a piece of fine and open weave linen canvas was placed between the wood and the ground after the fourteenth century. When the gesso had dried, the panel was sanded down to create an ivory-like finish and then the painting process could begin.

As already mentioned above,<sup>46</sup> the icon painters were following very firmly fixed iconographic rules, for their main role was to transmit and therefore to illustrate a holy message. Thus, prototypes were passed down from generation to generation, first by word of mouth and then by drawings and printed manuals, so that painters could copy them, with the possibility of any subjective expression strictly excluded.<sup>47</sup> Work was carried out chiefly in monasteries and church workshops, where monks would generally be subjected to long hours of prayer and fasting before being able to undertake the important task of painting an icon.<sup>48</sup>

Sendler notes that the first stage in the painting process was the preliminary underdrawing of the scene to be depicted, which was transferred into the gesso following the predetermined models. The pigments used for the preparation of the colours were mostly natural materials including mineral compounds and vegetable extracts, for example yellow and red ochres, red lakes, umber, minium, white lead, bone black, indigo, ultramarine, green earth etc., while a few manufactured pigments were also used such as vermilion and verdigris. These were first ground with water to a wet paste and then mixed together with the medium as they were applied. The execution of an icon began from the background, which could be either painted or gilded.<sup>49</sup>

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<sup>45</sup> For the very finest icons, a fine alabaster powder was sometimes used for the preparation of the gesso ground. See BAGGLEY, J., *Doors of Perception - Icons and Their Spiritual Significance*, St. Vladimir's Seminar Press, N. York (1995), p. 102.

<sup>46</sup> See p. 25

<sup>47</sup> SENDLER, E., *The Icon: Image of the Invisible*, translated by Fr. S. Bigham, Oakwood Publications (1988), p. 60-61.

<sup>48</sup> BAGGLEY, J., *Doors of Perception - Icons and Their Spiritual Significance*, St. Vladimir's Seminar Press, N. York (1995), p. 54-76.

<sup>49</sup> The gilding techniques will be discussed further in the next chapter.

The background colours that constituted the deepest shadows of the landscape, architecture, furnishings, garments and figures followed, <sup>50</sup> on top of which the layers of lights were gradually built up, <sup>51</sup> passing from the cooler and darker tones to the warmer and lighter ones. The final stage was the highlights of the faces, hands, hair and clothing, <sup>52</sup> as well as the various details of the composition, such as haloes, letters, golden decorative patterns and panel borders. After the passage of a few months, a film of varnish was applied, which protected the painted surface and also saturated the colours of the different paint layers. <sup>53</sup> At the end of this long procedure the icon was left in the sanctuary for forty days before receiving the final blessing from the priest, after which it could be either placed on the iconostasis (or a lectern) of the church or hung at the special icon corner of the house. <sup>54</sup>

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<sup>50</sup> These are called “προπλάσμοι” (proplasmoi).

<sup>51</sup> These are called “σαρκώματα” (sarkomata) and “γλυκασμοί” (glykasmoi).

<sup>52</sup> These include the “ψιμμιθιές” (psymmithies) and the “γραψίματα” (grapsimata).

<sup>53</sup> SENDLER, E., *The Icon: Image of the Invisible*, translated by Fr. S. Bigham, Oakwood Publications (1988), p. 193-238.

<sup>54</sup> In Greek this corner is also called the “iconostasis”.

### **C. Wall Paintings: Function, Evolution, Technology**

The art of Byzantine mural painting is an integral part of another great achievement of combined Byzantine architecture and the Christian religion: the church. Without churches wall paintings would hardly have existed, for the character of this form of art is again purely religious. While the exterior of those buildings was quite plain, based on bricks and tiles, their interior walls were entirely covered with either mosaics or mural paintings.<sup>55</sup> The principle that led the Byzantine artists to adopt mural decoration was the idea that the embellishment of the church would also glorify God.<sup>56</sup> With the establishment of the doctrine of Eastern Orthodoxy, wall paintings assumed a dogmatic and educational role. Churches developed an elaborate programme of decoration that featured the whole Bible, from the wonders of the Old Testament and Jesus Christ the Pantocrator, to His miracles and the twelve feasts of the church. This instructed the faithful, especially the illiterate, in the story of the salvation of man.<sup>57</sup> In addition, there was an evident desire to astonish the visitor with the impressive décor that, combined with the whole evocative atmosphere, would set him to the right state of mind to follow the ritual of the service.<sup>58</sup>

The first examples of religious mural paintings belong to regions that played an essential role in the general development of Byzantine art, but almost nothing of that early age has survived on purely Byzantine soil. Accordingly, from the period between the third and the ninth centuries the Roman art of catacomb painting must be noted, with its famous symbolic creations like that of the fish or the peacock, while certain

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<sup>55</sup> SENDLER, E., *The Icon: Image of the Invisible*, translated by Fr. S. Bigham, Oakwood Publications (1988), p. 68.

<sup>56</sup> Ibidem, p. 60.

<sup>57</sup> Ibidem, p. 67.

<sup>58</sup> Ibidem, p. 60.

representations such as the “Orans”<sup>59</sup> also derive from those early Christian years.<sup>60</sup> Of considerable interest are also the Coptic wall paintings, where both the Hellenistic and the Syrian or Semitic influences are evident.<sup>61</sup> From the *Middle Byzantine* era (843-1204 A.D.) there exist very few monuments in Byzantine territory and almost none in Constantinople. It is worthwhile, however, touching on the monastic art developed in Cappadocia during this period, with the mural paintings of the rock-cut chapels and the built churches constituting its most characteristic examples.<sup>62</sup>

By the second half of the twelfth century a general artistic revival occurred and a new painting manner arose. This evolution was manifested in the art of mural painting with the introduction of a number of new themes in the iconographic programme of churches, while at the same time artists paid much more attention to achieving an elaborate representation of all scenes.<sup>63</sup> After the Latin conquest and for the next century or so, painters that had left Constantinople worked in scattered churches, thus conveying the Constantinopolitan style to the provinces. Again, this study will only follow the development of mural painting in the Greek world as this appears to be the most significant of all, probably due to the fact that the Greek region formed the main body of the Byzantine world.

The period between the thirteenth and the sixteenth centuries is of primary importance, with the distinction of the Macedonian and the Cretan schools evident throughout the whole Greek territory. Some of the finest examples of these two manners can be found in the churches of Mystra in Peloponnese, Mount Athos in Chalkidiki and Meteora in Central Greece. The most important painter associated with the

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<sup>59</sup> A figure in frontal pose with the arms upraised in prayer.

<sup>60</sup> SENDLER, E., *The Icon: Image of the Invisible*, translated by Fr. S. Bigham, Oakwood Publications (1988), p. 12-14.

<sup>61</sup> TALBOT RICE, D., *Art of the Byzantine Era*, Thames & Hudson Ltd, London (1963), p. 24-28.

<sup>62</sup> Ibidem, p. 134-137.

<sup>63</sup> CORMACK, R., *Byzantine Art*, Oxford University Press, Oxford (2000), p. 175-179.

Macedonian school in Mount Athos and in the region of Salonica is *Manuel Panselinos*, whereas *Theophanes the Cretan* is the most famous representative of the Cretan school in both Mount Athos and Meteora.<sup>64, 65</sup> From the seventeenth century onwards wall paintings were created throughout the entire Orthodox world, but were generally of low quality and deprived of any spirit of innovation, owing to the general tendency of painters to copy the old masterpieces.

Byzantine churches were built with bricks and stones, which constituted the carrier of wall paintings too. The masonry, however, was too uneven to be used without preparation and for this reason it was covered with a ground of plaster. The main ingredients of the Byzantine wall painting plasters were lime and sand with the addition of certain organic materials, such as chopped straw, hemp and flax.<sup>66</sup> Yet in medieval mural painting other materials could be also used according to the number of layers applied. Hence, if the wall was too rough, pounded bricks were added to the first coatings to give the mortar more bulk. For the last plaster layers a larger amount of lime was used, mixed with finer sand and sometimes with marble dust to obtain an even and smooth painting surface.<sup>67</sup> With the evaporation of water from the mixture and the drying of the plaster, the lime forms crystals around the sand ensuring cohesion. In the course of time, however, the calcium hydroxide (lime) is converted to calcium carbonate due to its reaction with carbon dioxide in the air.<sup>68</sup>

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<sup>64</sup> TALBOT RICE, D., *Art of the Byzantine Era*, Thames & Hudson Ltd, London (1963), p. 252-261.

<sup>65</sup> DRANDAKI, A., *Greek Icons: 14<sup>th</sup>-18<sup>th</sup> Century – The Rena Andreadis Collection*, translated by J. Avgherinos, Skira (2002), p. 5.

<sup>66</sup> *The 'Painter's Manual' of Dionysius of Fourni*, translated into English by P. Hetherington, Oakwood Publications (1996), p. 12-16.

<sup>67</sup> THOMPSON, D.V., *The Materials and Techniques of Medieval Paintings*, Dover Publications, New York (1977), p. 38-40.

<sup>68</sup> MAYER, R., *The Artist's Handbook of Materials and Techniques*, Faber and Faber, 5<sup>th</sup> Edition (1991), p. 372-373.

According to Thompson <sup>69</sup> and Winfield <sup>70</sup>, the standard vehicle for medieval and Byzantine mural painting was lime that, when converted to calcium carbonate with the same mechanism described above, incorporated the pigment particles and became their binding medium. This action could be achieved in three different ways, which also designate three different techniques of mural painting. One was to mix the pigments with water and to apply them onto the fresh plaster, leaving the lime to act as binder and allowing the pigments to dry with it. This method is called “*fresco painting*” and most probably derived from the technique of mosaic painting practised in Byzantine art since the early centuries. <sup>71, 72</sup> The other method was to mix limewater or a little lime with the pigments before applying them onto the semi-dry or dried plaster, which had been previously dampened. These techniques are known as “*semi-secco painting*” and “*lime painting*” respectively and resulted in the creation of a surface paint layer, more or less detached from the plaster layer itself. To supplement the techniques, egg tempera was also used at the last stage of wall painting, for the purpose of reinforcing the details of the compositions and of applying the final highlights on the figures. This method is known as “*secco painting*” and had been put into practice in Byzantine mural painting also by using different binding media, for example glue and casein. <sup>73</sup>

The execution of a Byzantine wall painting, in terms of the actual painting process, resembles that of an icon and that is the reason why it was quite common to have the same painters working in both techniques. The major difference, however, was the scale of the painting

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<sup>69</sup> THOMPSON, D.V., *The Materials and Techniques of Medieval Paintings*, Dover Publications, New York (1977), p. 68-73.

<sup>70</sup> WINFIELD, D.C., *Middle and Later Byzantine Wall Painting Methods - A Comparative Study*, *Dumbarton Oaks Papers*, 22 (1968), p. 61-139.

<sup>71</sup> MAYER, R., *The Artist's Handbook of Materials and Techniques*, Faber and Faber, 5<sup>th</sup> Edition (1991), p. 365.

<sup>72</sup> LAURIE, A.P., *The Painter's Methods and Materials*, Dover Publications, Inc., New York (1967), p. 191-199.

<sup>73</sup> WINFIELD, D.C., *Middle and Later Byzantine Wall Painting Methods - A Comparative Study*, *Dumbarton Oaks Papers*, 22 (1968), p. 131-139.

surface. Given the limitation of time, painters used to divide the walls into horizontal bands from the vaults downwards, which corresponded to scaffolding lifts, and to make the plaster joints coincide with the decorative borders of the scenes. This horizontal plastering technique is known in Italian mural painting as division into “*pontate*”.<sup>74</sup> Finally, many of the pigments used in icons were also used in mural painting, with the exception of some of them that, when mixed with lime, altered their chemical composition as a reaction to its alkalinity, resulting in alteration of their original colour. The most typical examples of this kind are azurite, malachite, white lead and cinnabar.<sup>75</sup>

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<sup>74</sup> WINFIELD, D.C., *Middle and Later Byzantine Wall Painting Methods - A Comparative Study*, Dumbarton Oaks Papers, 22 (1968), p. 69-71.

<sup>75</sup> MAYER, R., *The Artist's Handbook of Materials and Techniques*, Faber and Faber, 5<sup>th</sup> Edition (1991), p. 139.



**GILDING: HISTORY AND TECHNOLOGY**

## A. Gold Leaf

Gold was one of the first metals that man learned how to manipulate because of its important property of malleability, thanks to which it can be easily beaten and formed into a desirable shape. <sup>1</sup> This, however, is not the only reason why gold, of all metals, became an integral part of many expressions of life and, in particular, art throughout the history of civilisations. Firstly, its value and fineness refer to power, richness, glory and honour and, secondly, its brilliant colour and the reflections it creates afford luminosity and gleam to any surface on which it is used. Furthermore, its noble metal stability and resistance to tarnish give durability to the objects on which it is applied and, finally, its adaptability and the flexibility with which it can be used to adorn small or larger areas render it an excellent material and the finest amongst metals for use in the decoration of works of art.

Two different terms have been employed to define metal sheets of varying thickness, composition and physical properties: foil and leaf. The former is generally used to describe a sufficiently thick sheet that can support its own weight while the latter, which mainly applies to gold, refers to a very thin sheet that has almost no weight and that can only be handled by specially designed tools. <sup>2</sup>

Gold is one of the few metals that can be gradually beaten out from a foil into an extremely thin, almost transparent leaf. Although some very early representations of gold-beating scenes have been found in ancient Egypt of the 6<sup>th</sup> Dynasty (about 2300 B.C.), <sup>3</sup> there exist very few written sources on the actual technique of producing gold leaf. The first-century

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<sup>1</sup> RAUB, C.J., *The Development of Gilding from Antiquity to the Middle Ages*, Materials Australasia, 18-19 (1986), p. 7.

<sup>2</sup> Ibidem, p. 7.

<sup>3</sup> HATCHFIELD, P., NEWMAN, R., *Ancient Egyptian Gilding Methods*, in *Gilded Wood: Conservation and History*, edited by D. Bigelow and C.E. Hutchins, Sound View Press, Madison, Connecticut (1991), p. 28.

A.D. military physician *Dioscorides* describes the use of copper plates between which gold foils were beaten to leaves.<sup>4</sup> The same method is mentioned in the late eighth-century so-called “*Lucca Manuscript*”.<sup>5</sup> There may, however, have been some variations, for instance the use of leather or parchment in the place of copper.<sup>6</sup> A more detailed explanation of the process of gold beating using this technique is found in the so-called “*Mappae Clavicula*”, a compilation that dates from the twelfth century.<sup>7</sup> In his treatise of the early twelfth century *Theophilus Presbyter* presents a different way of making gold leaf not by using copper plates, but by utilising a sort of pouch made of calf parchment. The gold foils were placed in it, interleaved with sheets of flax-made paper, and were then beaten into leaves.<sup>8</sup>

Although some innovations have been introduced in gold beating in modern times, especially during the last century, the majority of the process seems to have remained unchanged. The gold is first cast in ingots and then rolled in continuous ribbons. The beating is achieved by piling up small squares of gold sheets laid between larger squares of a special kind of parchment (goldbeaters’ skin). Then the sheets are hammered until the gold is spread out to the edges of the skins and the same process repeated.<sup>9</sup> Before the beating, the skins are rubbed with calcined gypsum (“brime” powder), while after beating the leaves are cut into squares on a padded leather cushion with a cane-bladed knife. The squares of gold leaf are then placed with the help of tweezers in books between specially prepared sheets of paper. Gold leaves were beaten by

<sup>4</sup> *Pedanii Dioscoridis Anazarbei de Materia Medica Libri Quinque*, edited by C.G. Kühn, Vol. 1, Lipsia 1829, p. 754 and THEOBALD, W., *Die Goldschlägerkunst im Altertum und Mittelalter*, Kunst und Kunsthandwerk, 14 (1911), p. 574. This technique is also described by Plinius in the same century (see note 16).

<sup>5</sup> *A Classical Technology Edited From the Codex Lucensis, 490*, edited by J.M. Burnam, The Gorham Press, Boston (1920), p. 98-99.

<sup>6</sup> THEOBALD, W., *Glaser's Annalen für Gewerbe und Bauwesen*, 833 (1912), p. 91.

<sup>7</sup> *Mappae Clavicula - A Little Key to the World of Medieval Techniques*, edited by C.S. Smith and J.G. Hawthorne, Transactions of the American Philosophical Society, New Series, Vol. 64, Part 4, The American Philosophical Society, Philadelphia (1974), p. 65.

<sup>8</sup> THEOPHILUS, P., *On Divers Art: The Treatise of Theophilus*, translated by J.G. Hawthorne and C.S. Smith, University of Chicago Press, Chicago (1963), p. 29.

<sup>9</sup> This pack is known as “cutch”.

hand until replaced by a mechanised hammering machine that uses plastic sheets instead of goldbeaters' skin in the 1920s.<sup>10</sup>

The standard modern gold leaf is 0.1  $\mu\text{m}$  ( $10^{-6}$  m) thick<sup>11</sup> and 8.3 cm square<sup>12</sup>. Although the size has remained more or less the same, in ancient and medieval times the thickness would vary substantially depending on the contemporary available technology. Thus in the gold coated findings of *Schliemann* in Troy from approximately 3100-2700 B.C., the thickness of the gold was a fraction of a millimetre ( $10^{-3}$  m).<sup>13</sup> In gilding samples taken from various Egyptian objects dating from 2600 B.C. to the fourth century A.D. the thickness varied from 10.4 to 0.65  $\mu\text{m}$ ,<sup>14</sup> whereas from the investigation of the gold coating of a Roman-Classic marble column, the leaf was found to be 2-3  $\mu\text{m}$  thick.<sup>15</sup> Furthermore, *Plinius* states in the thirty-third book of his first-century A.D treatise: "... an ounce of gold can be beaten out into 750 or more leaves 4 inches square";<sup>16</sup> this corresponds to a gold leaf of 10 cm square and 0.5  $\mu\text{m}$  thick. It is stated in the "*Mappae Clavicula*", however: "...Repeat this until out of the [original] 8 leaves 1028 are made".<sup>17</sup> This is equivalent to a thickness of around 6  $\mu\text{m}$ , namely a leaf much thicker than those produced in earlier times and sixty times the thickness of a modern gold leaf.

<sup>10</sup> MACTAGGART, P. & A., *Practical Gilding*, Mac & Me Ltd (1995), p. 1-4.

<sup>11</sup> RAUB, C.J., *The Development of Gilding from Antiquity to the Middle Ages*, Materials Australasia, 18-19 (1986), p. 7.

<sup>12</sup> MACTAGGART, P. & A., *Practical Gilding*, Mac & Me Ltd (1995), p. 2.

<sup>13</sup> RAUB, C.J., *The Development of Gilding from Antiquity to the Middle Ages*, Materials Australasia, 18-19 (1986), p. 7.

<sup>14</sup> HATCHFIELD, P., NEWMAN, R., *Ancient Egyptian Gilding Methods*, in *Gilded Wood: Conservation and History*, edited by D. Bigelow and C.E. Hutchins, Sound View Press, Madison, Connecticut (1991), p. 30-33.

<sup>15</sup> RAUB, C.J., *The Development of Gilding from Antiquity to the Middle Ages*, Materials Australasia, 18-19 (1986), p. 8.

<sup>16</sup> PLINIUS C. SECONDUS, *Natural History* in Ten Volumes, with an English translation by H. Rackham, Volume IX, Libri XXXIII-XXXV, William Heinemann, London (1968), p. 49.

<sup>17</sup> *Mappae Clavicula - A Little Key to the World of Medieval Techniques*, edited by C.S. Smith and J.G. Hawthorne, Transactions of the American Philosophical Society, New Series, Vol. 64, Part 4, The American Philosophical Society, Philadelphia (1974), p. 65.

The Florentine *Cennino Cennini* wrote in his manual “*Il Libro dell’Arte*” at the end of the fourteenth century: “... *for the gold which is laid on flats they ought not to get more than a hundred leaves out of a ducat, whereas they do get a hundred and forty-five*”.<sup>18</sup> This reveals that in Florence, as well as in the other two most important gold-coinage centres, Venice and Genoa, gold coins were used for leaf beating during the Italian Renaissance, called respectively florin, ducat and genoven.<sup>19</sup> All these were of pure 24-carat gold and weighed exactly the same. Therefore, by combining Cennini’s piece of information on the production of one hundred leaves out of a ducat with the varying weight of those coins throughout the years (3.33-3.52 g) and the density of gold (19.3 g/cm<sup>3</sup>), it is possible to calculate the thickness of a gold leaf at the time; for an approximate surface of 7.3-8 cm square, it ranged from 0.269 to 0.325 µm.<sup>20, 21</sup> This seems to have been the ideal thickness according to Cennini, but still the gold leaf produced today results in being half to one third this thickness.

The purity of gold is measured in “carats” (ct), with the purest being 24 ct, while any lower figure means that the metal concerned is an alloy.<sup>22</sup> The composition of gold leaf may vary widely owing to many factors. Native gold ore contains other metals as well, such as silver and copper. Nevertheless, the introduction of purification processes of gold in Mesopotamia at around 2000 B.C. made the production of extremely

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<sup>18</sup> CENNINI, C., *The Craftsman's Handbook - The Italian 'Il Libro dell'Arte'*, translated by D.V. Thompson, Dover Publications, Inc., New York (1960), p. 84.

<sup>19</sup> MERZENICH C., *Dorature e Policromie delle Parti Architettoniche nelle Tavole d'Altare Toscane Fra Trecento e Quattrocento*, Kermes: Arte e Tecnica del Restauro, 26 (1996), p. 55-57.

<sup>20</sup> BOMFORD, D., DUNKERTON, J., GORDON, D., ROY, A., *Art in the Making: Italian painting before 1400: Exhibition Catalogue, London, 29 November 1989 - 28 February 1990*, National Gallery, London (1989), p. 22.

<sup>21</sup> MERZENICH C., *Dorature e Policromie delle Parti Architettoniche nelle Tavole d'Altare Toscane Fra Trecento e Quattrocento*, Kermes: Arte e Tecnica del Restauro, 26 (1996), p. 57.

<sup>22</sup> MACTAGGART, P. & A., *Practical Gilding*, Mac & Me Ltd (1995), p. 2-3.

pure gold feasible.<sup>23</sup> Occasionally, however, intentional alloying takes place in order to increase the hardness and durability of the gold and to achieve a great variety of colours. Thus, the presence of copper results in a reddish gold, added silver yields a white gold and, depending on the different alloys, a multitude of colours can be obtained, such as grey, blue, green, lemon, yellow, orange, pink etc. The alloying with inferior and cheaper metals, mainly tin and copper, is an alternative to the costly gold leaf. Gold can also be imitated by using white metals such as silver and tin, lacquered with yellow-tinted varnish or yellow pigments. It should also be noted that the thickness of the leaf produced is not dependent on the purity of the gold available.<sup>24</sup>

In today's manufacture, apart from the standard or "single-weight" gold leaf, thicker "double-weight" or "triple-weight" leaves are also available and quadruple gold can sometimes be found. In addition, gold leaf is supplied in two different forms, called respectively "loose" and "transferred". In the first case the leaves are simply placed in a book between sheets of paper, from where they can be easily removed, whereas in the second case they are attached and therefore secured with wax to larger sheets of tissue paper.<sup>25</sup> These two types of gold leaf are used in the different gilding techniques that will be further discussed in the following section.

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<sup>23</sup> RAUB, C.J., *The Development of Gilding from Antiquity to the Middle Ages*, Materials Australasia, 18-19 (1986), p. 7.

<sup>24</sup> CESSION, C., *The Surface Layers of Baroque Gildings: Examination, Conservation, Restoration*, in *Cleaning, Retouching and Coatings: Technology and Practice for Easel Paintings and Polychrome Sculpture, Preprints of the Contributions to the Brussels Congress, 3-7 September 1990*, edited by J.S. Mills and P. Smith, International Institute for Conservation of Historic and Artistic Works, London (1990), p. 33-35.

<sup>25</sup> MACTAGGART, P. & A., *Practical Gilding*, Mac & Me Ltd (1995), p. 3.

## **B. Gilding from Antiquity to Western European Painting**

Gilding, namely the technique of applying a thin sheet of gold over a firm support, is a practice that comprises a multitude of different methods, which can be carried out on a great variety of substrate materials. A few examples of them will only be stated, such as fire or amalgam gilding, chloride of gold gilding, honey gilding, fused gilding, “eglomisé”, depletion gilding, electrochemical gilding, electro-plating etc. This essay, however, will only focus on the technique of gilding with leaf over wooden and mural surfaces.

The craft of gilding on wood and plaster appears to have originated in Egypt more than 4000 years ago, where gilded wooden objects and mummy masks were created.<sup>26</sup> Gold-coated objects that date back to earlier times have also been found, for example the findings of Troy from about 3000 B.C. The use of gold leaf in mural painting, however, only became popular in the Hellenistic and, later, in the Roman age, where it was occasionally applied on painted and stucco decorations to accentuate certain details, particularly on ceilings.<sup>27, 28</sup>

In Western Europe the technique of gilding with leaf on paintings, as well as on polychrome sculptures, appeared in the eleventh and was established in the twelfth century, i.e. in the Romanesque period. The climax, however, was reached between the fourteenth and eighteenth centuries, i.e. the late medieval and the Baroque periods.<sup>29</sup> Gilding is

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<sup>26</sup> HATCHFIELD, P., NEWMAN, R., *Ancient Egyptian Gilding Methods*, in *Gilded Wood: Conservation and History*, edited by D. Bigelow and C.E. Hutchins, Sound View Press, Madison, Connecticut (1991), p. 27-47.

<sup>27</sup> PLINIUS C. SECONDUS, *Natural History* in Ten Volumes, with an English translation by H. Rackham, Volume IX, Libri XXXIII-XXXV, William Heinemann, London (1968), p. 47.

<sup>28</sup> MACKENNA S. A., LING R., *Wall Paintings from the Winchester Palace Site, Southwark*, Britannia, 22 (1991), p. 159-171.

<sup>29</sup> SERCK-DEWAIDE, M., *The History and Conservation of the Surface Coating on European Gilded-Wood Objects* and WESTHOFF, H., *Coatings of Medieval Gilded Surfaces and their Deterioration*, in *Gilded Wood: Conservation and History*, op. cit. p. 65-78 & 79-86.

particularly associated with fourteenth-century Italian painting, yet it continued to be widely used in Italy during the Renaissance and remained in practice until the sixteenth century. It also played an important role in the Netherlandish, German, and the Spanish painting of the same period.<sup>30</sup> In the Baroque era gilding became diversified with a vast range of variations in the imitation techniques applied, the alloys used and the effects of the colours and contrasts obtained.<sup>31</sup> A characteristic example of this is the Baroque-style furniture that flourished in France under the reign of *Louis XIV* (1643-1715 A.D.).<sup>32</sup> *Jean-Félix Watin* in his treatise “*L’ Art du Peintre, Doreur, Vernisseur*” describes in minute detail all the gilding techniques developed in that age.<sup>33</sup>

The application of gold leaf on a surface is a very delicate operation and requires dexterity and practical expertise. The Egyptians from as early as 3000 B.C. used to wrap objects with gold foil, either with or without adhesive, and then secured it by folding its edges.<sup>34</sup> A similar method was also employed in the Classic and Roman periods, where several objects were found to have been gold-coated with the foil bent over their ends and hammered into specially cut grooves,<sup>35</sup> a technique

<sup>30</sup> DUNKERTON, J., FOISTER, S., GORDON, D., PENNY, N., *Giotto to Dürer: Early Renaissance Painting in the National Gallery*, National Gallery Publications, London (1991), p. 174-182 & 397.

<sup>31</sup> CESSION, C., *The Surface Layers of Baroque Gildings: Examination, Conservation, Restoration*, in *Cleaning, Retouching and Coatings: Technology and Practice for Easel Paintings and Polychrome Sculpture*, Preprints of the Contributions to the Brussels Congress, 3-7 September 1990, edited by J.S. Mills and P. Smith, International Institute for Conservation of Historic and Artistic Works, London (1990), p. 33-35.

<sup>32</sup> CONSIDINE, B.B., *The Gilders Art in Eighteenth-Century France*, in *Gilded Wood: Conservation and History*, edited by D. Bigelow and C.E. Hutchins, Sound View Press, Madison, Connecticut (1991), p. 87-98.

<sup>33</sup> WATIN, J.F., *L’Art du Peindre, Doreur, Vernisseur*, 4<sup>th</sup> Edition, Paris (1787).

<sup>34</sup> HATCHFIELD, P., NEWMAN, R., *Ancient Egyptian Gilding Methods*, in *Gilded Wood: Conservation and History*, edited by D. Bigelow and C.E. Hutchins, Sound View Press, Madison, Connecticut (1991), p. 34.

<sup>35</sup> ODDY, W.A., BORELLI VLAD, L., MEEKS, N.D., *Die Vergoldung von Bronzestatuen bei den Griechen und Romern*, in *Die Pferde von San Marco: Exhibition Catalogue*, 8 March-25 April 1982, Frölich & Kaufmann, Berlin (1982), p. 107.



that is also mentioned by Plinius.<sup>36</sup> However, the use of intermediary grounds such as gesso and plaster was also introduced during that period. Plinius describes that the white of an egg was used for laying gold on materials such as marble and possibly masonry as well. For gilding on wood he recommends a sort of cement called “leucophorum” (i.e. white-bearing), made of a mixture of sinoper from Pontus, yellow ochre and earth from the Greek island of Melos and applied with glue, most likely again egg white.<sup>37</sup>

In Western European panel painting two main techniques have been developed from the early Middle Ages: water and mordant gilding. In the preparation of a panel, water gilding was the stage that followed the preliminary drawing on the gesso ground and preceded the actual painting, while mordant gilding was the final phase of the execution of a painting. The division between the areas to be gilded and those to be painted was usually made by lines that were gently incised into the gesso by means of a stylus.<sup>38</sup>

Bomford *et al.* explain that in water gilding in the majority of cases the gold leaf was applied onto a specially prepared ground that consisted of bole and glair or weak size (e.g. plain egg white or animal glue). Bole is a soft, smooth and greasy red-brown clay (an aluminium-silicate containing ferric oxide) that, together with the underlying gesso, acts as a cushion against which the gold could be burnished. Furthermore, its colour affected the final appearance of the gilding by conferring a tone to the slightly transparent gold. Glair is the white of an egg that is whisked to foam and then left to liquefy again with or without added water. The bole, usually available in the form of lumps,

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<sup>36</sup> PLINIUS C. SECONDUS, *Natural History* in Ten Volumes, with an English translation by H. Rackham, Volume IX, Libri XXXIII-XXXV, William Heinemann, London (1968), p. 61.

<sup>37</sup> Ibidem, p. 51 & 287.

<sup>38</sup> BOMFORD, D., DUNKERTON, J., GORDON, D., ROY, A., *Art in the Making: Italian painting before 1400: Exhibition Catalogue*, London, 29 November 1989 - 28 February 1990, National Gallery, London (1989), p. 21-26 & 43-47.

was first ground with water, then mixed with the glair or the weak size and finally applied onto the gesso ground in several layers. When dry, it was lightly burnished, as described below, or merely polished with a linen cloth in order to create a reflective surface of high sheen. The panel was then ready for gilding. If necessary, the gold leaf was cut to the desired size on a leather cushion using a special knife and then picked up with a gilder's tip, i.e. a very thin, very wide brush. The bole was first wetted with plain water or with a mixture of water and a little glair for the purpose of reactivating the original binder (glair or weak size), hence the term "*water gilding*". Thus, when the gold leaf was laid onto its surface, it was attached to it and then tapped down with a pad to secure the adhesion. Any small cracks and flaws that appeared were covered with scraps of gold.

On completion of this process the gold looks matt and crinkled, with the edges of the leaves overlapping one another. In order for the gilding to acquire a bright shiny aspect, the gold had to be burnished. Bomford *et al.* note that the burnishing was performed by using either a hard polished stone, such as agate, precious stones like sapphires, emeralds and rubies, or the cheaper alternative of an animal tooth. Once it was completed artists often proceeded to create various patterns, especially on the haloes and the background borders for the purpose of ornamenting further the gilded surface. These included incised lines, tooling and punching, a procedure that will not be further analysed in this context. The technique of water gilding has been elaborately described by Cennino Cennini in his treatise.<sup>39</sup>

Medieval and early Renaissance painters, however, did not always use bole as ground for the gilding but, seeking to create different chromatic effects, they often chose to apply gold either over a layer of

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<sup>39</sup> CENNINI, C., *The Craftsman's Handbook - The Italian 'Il Libro dell'Arte'*, translated by D.V. Thompson, Dover Publications, Inc., New York (1960), p. 79-86.

green earth or directly onto the white gesso.<sup>40, 41, 42</sup> During the Baroque period, when gold leaf became thinner as a result of improved gold-beating techniques, the tone of the gilding ground played a significant role on the final colour of the gold. Apart from the orange-red bole that was characteristic of that period, clays of various colours were also used, such as dark red, yellow, brown, green, white etc. In addition to that, the contrast between the areas where gold has been burnished and those where it was remained matt enhanced the richness of the decorative potential.<sup>43</sup>

After the painting of the panel had been completed, the final stage was the embellishment of draperies with lines and motifs of gold, which were executed using the refined technique of “*mordant gilding*”. Bomford *et al.* explain that small pieces of gold leaf were attached onto the areas to be adorned by means of an adhesive or so-called “mordant”. There are many different types of mordants made of various materials, but the standard form consisted of an oleo-resinous composition that possesses the property of developing a considerable degree of tackiness. In this case the technique is more specifically called “*oil gilding*”.<sup>44</sup> The mordant was first painted out, often in rather thick, raised lines, and left to dry slightly. Then the gold leaf was cut to the right size and laid over the mordant while this was still sticky. Any leftover scraps of gold were reused or brushed away and the panel was then ready for varnishing. Mordant gilded surfaces remained matt as the gold was laid over a hard layer of mordant rather than over a soft ground of bole and

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<sup>40</sup> Ibidem, p. 80.

<sup>41</sup> BOMFORD, D., DUNKERTON, J., GORDON, D., ROY, A., *Art in the Making: Italian painting before 1400: Exhibition Catalogue, London, 29 November 1989 - 28 February 1990*, National Gallery, London (1989), p. 69.

<sup>42</sup> DUNKERTON, J., FOISTER, S., GORDON, D., PENNY, N., *Giotto to Dürer: Early Renaissance Painting in the National Gallery*, National Gallery Publications, London (1991), p. 174, 212-215 & 266-267.

<sup>43</sup> See note 31.

<sup>44</sup> See CESSION, C., *op. cit.*, p. 33-35.

therefore could not be easily burnished.<sup>45</sup> Details about the mordant gilding technique and the technology of oil mordants will be set out in subsequent chapters, as these issues constitute the main subject of the present study.

A more elaborate method of gilded ornamentation that made use of the mordant gilding technique is the so-called “*pressed brocade*” or “*applied relief gilding*”. It is a relief decoration made of pre-formed raised patterns, which were attached to the gesso ground, gilded using an oil-based mordant and then painted.<sup>46</sup> This technique is frequently encountered in Northern European polychromed sculpture and panel painting and was chiefly used for the execution of cloths and textiles of gold in imitation of golden embroidery.<sup>47, 48</sup> Another method of adorning fabrics with gold was the fourteenth-century Italian technique of “*sgraffito*”; above the burnished water-gilded surface a paint layer was applied and then removed by scratching with a wooden or bone scraper. This resulted in the reappearance of the underlying gold following specially designed motifs.<sup>49, 50</sup> The technique of “*shell gold*”, namely powdered gold made by grinding up gold leaf with glair and applied with

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<sup>45</sup> BOMFORD, D., DUNKERTON, J., GORDON, D., ROY, A., *Art in the Making: Italian painting before 1400: Exhibition Catalogue*, London, 29 November 1989 - 28 February 1990, National Gallery, London (1989), p. 43-47.

<sup>46</sup> Raised decoration patterns created onto the gesso ground were also in frequent use. The so-called “*pastiglia*”, made of gypsum or chalk mixed with glue, were usually water-gilded. See CENNINI, C., *The Craftsman's Handbook - The Italian 'Il Libro dell'Arte'*, translated by D.V. Thompson, Dover Publications, Inc., New York (1960), p. 76.

<sup>47</sup> RICHARDSON, R., *The History and Techniques of Pressbrokaat*, in *Gilding and Surface Decoration. Preprints of the UKIC Conference Restoration '91*, edited by S. Budden, London (1991), p. 36-39.

<sup>48</sup> SERCK-DEWAIDE, M., *Relief Decoration on Sculptures and Paintings from the Thirteenth to the Sixteenth Century: Technology and Treatment*, in *Cleaning, Retouching and Coatings: Technology and Practice for Easel Paintings and Polychrome Sculpture, Preprints of the Contributions to the Brussels Congress, 3-7 September 1990*, edited by J.S. Mills and P. Smith, International Institute for Conservation of Historic and Artistic Works, London (1990), p. 36-40.

<sup>49</sup> CENNINI, C., *The Craftsman's Handbook - The Italian 'Il Libro dell'Arte'*, translated by D.V. Thompson, Dover Publications, Inc., New York (1960), p. 86-88.

<sup>50</sup> PLESTERS, J., ROY, A., *The Materials and Technique: Cennino Cennini's Treatise Illustrated*, National Gallery Technical Bulletin, 9 (1985), p. 29-30.

the brush as a pigment, was also employed for the decoration of panels and manuscripts, predominantly during the fifteenth century.<sup>51</sup>

In mural painting the embellishment with gold was limited to just a few details of the painted figures, such as haloes and garments. For the application of gold leaf on mural surfaces the mordant gilding technique was generally in use<sup>52</sup> together with other variants, like that of the “*laminated gilding*”. According to this method, a tin foil approximately 10-20 µm thick was applied, to act as ground, either directly in contact with the wall plaster or over a layer of yellow ochre painted “*a fresco*” or even over a coat of beeswax. The adhesion was obtained by means of an oil mordant similar to that used on panels. The gold leaf was then attached using a very thin layer of the same type of mordant. Hence, the whole laminated leaf gained a consistent thickness, as well as pliancy and durability, avoiding the irregularity of the mortar underneath and permitting the gilding to acquire an even, smooth surface. Burnishing, together with other decorative techniques, could be performed on this support, for example punching and tooling. The lamination technique was mainly employed in areas of extensive gilded adornments, such as haloes, where the effect of burnished and punched gold was required and where the cost of using a thick gold leaf could not be met.<sup>53, 54</sup>

In some cases shell gold was also used, particularly in very fine patterns where the mordant gilding technique was not sufficiently effective. A more elaborate examination of the mural gilding decoration will be presented in the next chapter.

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<sup>51</sup> CENNINI, C., op. cit., p. 102. The gold produced in that way was traditionally kept in a mussel or similar shell, hence the term “*shell gold*”.

<sup>52</sup> MERRIFIELD, M.P., *The Art of Fresco Painting as Practised by the Old Italian and Spanish Masters*, A. Tiranti, London (1966), p. 110-111.

<sup>53</sup> CENNINI, C., *The Craftsman's Handbook - The Italian 'Il Libro dell'Arte'*, translated by D.V. Thompson, Dover Publications, Inc., New York (1960), p. 61-62.

<sup>54</sup> MATTEINI, M., MOLES, A., *Le Tecniche di Doratura nella Pittura Murale in Le Pitture Murali: Tecniche, Problemi, Conservazione*, Opificio delle Pietre Dure, Centro Di, Florence (1990), p. 121-126 and *Tecniche della Pittura Antica: Le Preparazioni del Supporto*, Kermes, 4 (1989), p. 61-62.

### C. Gilding in Byzantine Iconography

The gilding of icons seems to have been introduced to Byzantium from the “*Fayum portraits*”, encaustic panel paintings created in Hellenistic and Roman Egypt.<sup>55</sup> Yet, it only came into broad use with the establishment of icons as the principal expression of Byzantine art, namely after the end of the iconoclastic period (726-843 A.D.). However, in mural painting, which was a form of art that flourished in Byzantium much later, gilded decoration was applied on a more limited scale.

Gold has been an integral part of Byzantine iconography, with its main role being to detach the depicted scenes and figures from the material world and to confer a divine provenance upon them.<sup>56</sup> It has been used for the backgrounds, a distinctive feature closely associated with the art of icon painting, as well as for the haloes and clothing of the sacred figures in both icons and wall paintings.

The gold leaves were produced, at least after the establishment of the mints and the issue of gold coins in Europe in the thirteenth century, by beating the Byzantine gold coins called “*solidi*”.<sup>57</sup> In icon painting during the Byzantine and Post-Byzantine periods, as in Western European painting for that matter, gold was applied using both the techniques of water and mordant gilding.<sup>58</sup>

The backgrounds of the icons were water-gilded and so were the haloes of the figures. The actual practical method of water gilding in

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<sup>55</sup> HATCHFIELD, P., NEWMAN, R., *Ancient Egyptian Gilding Methods*, in *Gilded Wood: Conservation and History*, edited by D. Bigelow and C.E. Hutchins, Sound View Press, Madison, Connecticut (1991), p. 386.

<sup>56</sup> OUSPENSKY, L., *Theology of the Icon*, Vol. II, St. Vladimir’s Seminary Press, N. York (1992), p. 495-496.

<sup>57</sup> KOSSOLAPOV, A.J., *Historical and Technical Aspects of Gilded Russian Icons*, in *Gilded Wood: Conservation and History*, edited by D. Bigelow and C.E. Hutchins, Sound View Press, Madison, Connecticut (1991), p. 183-192.

<sup>58</sup> See SENDLER, E., *The Icon: Image of the Invisible*, translated by Fr. S. Bigham, Oakwood Publications (1988), p. 194-196. The Greek term “*χρυσοκονδυλίδ*” (*chrysokondylia*) is also employed to describe the latter.

Byzantium, however, does not always seem to correspond to the main Western European technique. In several cases the intermediate ground of bole was not used; the leaf was attached with glair directly onto the well-polished gesso and it gained a cool tone accordingly. Occasionally one or more background layers of fine ochre were painted first over the gesso to yield a warmer tone. The fact that this particular method of water gilding was used during the Byzantine period is confirmed by Theophilus Presbyter, identified as the metalworker *Roger of Helmarshausen*, in his twelfth century treatise. Although not written on Byzantine soil, as the author was from Helmarshausen, Germany, this manual has a Byzantine bias and the Byzantine pseudonym, “Theophilus”, chosen by the Benedictine monk implies recognition of the Byzantium’s excellence in the techniques he describes. The absence of bole, however, did not preclude burnishing, as Theophilus himself proposes the application of one or two more gold leaves on top of the first for the purpose of attaining a brighter burnished surface.<sup>59</sup> Another medieval document that confirms the use of metal foils applied directly onto the gesso ground of medieval European paintings in is the so-called “*Líkneskjusmíð*”, a short fourteenth century Icelandic text on the technique of painting.<sup>60</sup>

According to another method of water gilding that appears to have been put also into practice by Byzantine icon painters, the gold leaf was laid over a thin ground of green earth tempered with either glair or plain egg white. Cennino Cennini in his treatise of the late fourteenth century refers to this method with the comment “... *as our forefathers used to do...*”, quite explicitly hinting at the Byzantine painters from whom the Italian masters of the thirteen and fourteenth centuries inherited the

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<sup>59</sup> THEOPHILUS, P., *On Divers Art: The Treatise of Theophilus*, translated by J.G. Hawthorne and C.S. Smith, University of Chicago Press, Chicago (1963), p. 31.

<sup>60</sup> PLAHTER, U., *Líkneskjusmíð: Fourteenth Century Instructions for Painting from Iceland*, *Zeitschrift für Kunsttechnologie und Konservierung*, 6 (1992), p. 171.

knowledge and the style of painting.<sup>61</sup> Obviously a burnished green-earth-gilded surface would have never obtained the same sheen as a bole-gilded surface. Nevertheless the painting acquired a characteristic, slightly granular appearance.<sup>62</sup>

As already mentioned, the two methods of water gilding described above have also been found in a few Northern European and Italian panels dating from the medieval and early Renaissance eras, obviously attributed to Byzantine influence.<sup>63</sup>

Nevertheless, water gilding on bole ground was widely introduced to icon painting during the Post-Byzantine period, despite the existence of much earlier examples of icons with bole-gilded backgrounds.<sup>64</sup> The only documentary source that describes the techniques applied in Byzantine painting is the so-called “*Hermeneia*”, compiled by the Greek monk and painter *Dionysius of Fournà* in between 1730 and 1734 A.D. In his manual, Dionysius refers to the method of laying gold leaf on icons and iconostases by recommending three different mixtures to be used as grounds; all three of them contain red bole and ochre of Constantinople. The additional materials are red lead, mercury, cinnabar, soap, tallow candle wax, gall and burnt paper. These were first tempered with egg white and then painted over the gesso. The spirituous Greek liqueur “raki”, made from mastic and aniseed, is also mentioned whereby the bole-based layer was moistened before the gold leaf was applied.<sup>65</sup>

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<sup>61</sup> CENNINI, C., *The Craftsman's Handbook - The Italian 'Il Libro dell'Arte'*, translated by D.V. Thompson, Dover Publications, Inc., New York (1960), p. 80 and *Il Libro dell'Arte*, a cura di F. Brunello, Neri Pozza Editore, Vicenza (1998), p. 134, note 1.

<sup>62</sup> BOMFORD, D., DUNKERTON, J., GORDON, D., ROY, A., *Art in the Making: Italian painting before 1400: Exhibition Catalogue, London, 29 November 1989 - 28 February 1990*, National Gallery, London (1989), p. 69.

<sup>63</sup> See note 40, 41& 42.

<sup>64</sup> HOENIGSWALD, A., *The 'Byzantine' Madonnas: Technical Investigation*, Studies in the History of Art, 12 (1982), p. 26-27.

<sup>65</sup> *The 'Painter's Manual' of Dionysius of Fournà*, translated into English by P. Hetherington, Oakwood Publications (1996), p. 7 and ΔΙΟΝΥΣΙΟΥ ΤΟΥ ΕΚ ΦΟΥΡΝΑ, *Ερμηνεία της Ζωγραφικής Τέχνης*, υπό Α. Παπαδόπουλου-Κεραμέως, Εκδόσεις Κ.Χ. Σπανού, Πετρούπολη (1909), p. 17-18.



In Byzantium the gold of the haloes and backgrounds was left plain and sometimes burnished to catch the light.<sup>66</sup> Later on, though, simple decorative motifs were punched onto the gold in line with the punch work of the Western European panel painting, but by using much more simple techniques. A typical example is the formation of indentations following a pre-designed sketch, in the voids of which painters often dripped a resinous material, thus creating dotted-like adornments.<sup>67</sup> As an alternative to gilding, the icon backgrounds and haloes were frequently covered with silver plaques that had been previously adorned with motifs in relief or mounted with enamels, pearls and precious stones.<sup>68</sup> Furthermore, gold and silver alloys were occasionally employed after the development of their production in Byzantium in the eleventh century. Shell gold also came into use possibly in the fifteenth century and during the Post-Byzantine period substitutes of gilding such as the twin-gold leaf (gold and silver sheets beaten together) or tin and silver foils were used as well, but on a much more limited scale.<sup>69</sup>

In icons, as in Western European paintings for that matter, the technique of mordant gilding was employed for the linear embellishment of the hems, folds and the cuffs of garments (cloaks, mantles and veils), the borders of draperies, books or other objects, as well as for the accentuation of certain details, for instance the three stars on the Virgin's mantle that symbolise eternal virginity. According to Belting, the system of gold lines on the draperies shaped into comb patterns and large patches that simulate the movement of the light was actually developed in Byzantium. Despite the apparent resemblance to the

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<sup>66</sup> BELTING, H., *The 'Byzantine Madonnas': New Facts About Their Italian Origin and Some Observations on Duccio*, *Studies in the History of Art*, 12 (1982), p. 12.

<sup>67</sup> HOENIGSWALD, A., *The 'Byzantine' Madonnas: Technical Investigation*, *Studies in the History of Art*, 12 (1982), p. 27 & 29, fig. 5.

<sup>68</sup> RAMOS-POQUI, G., *The Technique of Icon Painting*, Burns & Oates/Search Press (1999), p. 48.

<sup>69</sup> KOSSOLAPOV, A.J., *Historical and Technical Aspects of Gilded Russian Icons*, in *Gilded Wood: Conservation and History*, edited by D. Bigelow and C.E. Hutchins, Sound View Press, Madison, Connecticut (1991), p. 183-192.

mordant-gilded decoration of the Western European paintings in terms of the method of execution and the particular areas where it was applied, ornaments in icons were much less complex. They were chiefly limited to simple flat lines, in contrast with the often striking raised lines of the Western panels, predominantly aiming to afford a symbolic character to the depicted scenes. In addition, the soft and flowing gold highlights in icons tend to dematerialise drapery, whereas in the West they are schematised into a more rigid system.<sup>70</sup>

In mural painting, gilded decoration seems to be executed using the mordant gilding technique in a similar method as in icons.<sup>71</sup> Moreover, the decorative scheme and the function of the gilding described above apply to murals as well. A more thorough approach and investigation of mordant-gilded panel and wall paintings in general and the materials used for the preparation of their mordants follows.

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<sup>70</sup> BELTING, H., *The 'Byzantine Madonnas': New Facts About Their Italian Origin and Some Observations on Duccio*, *Studies in the History of Art*, 12 (1982), p. 10.

<sup>71</sup> See WINFIELD, D.C., *Middle and Later Byzantine Wall Painting Methods - A Comparative Study*, *Dumbarton Oaks Papers*, 22 (1968), p. 133.

**MORDANT GILDING IN PANEL AND MURAL  
PAINTING**

## A. Primary Sources

Information about the techniques and materials used by the painters of the past can be gained in two ways; firstly, from documentary sources and secondly, from examination of the paintings themselves. The technique of mordant gilding has been the principal or secondary subject of a number of studies that have been published to date. Moreover, a considerable number of extant historical sources on the painter's craft, in the form of manuals, treatises, monographs and compilations, touch on the use of mordants in relation to the adhesion of gold leaf on paintings. These records, however, as well as the other published works, are restricted to art objects hailing from a Western European context, where painting was based upon different principles from those encountered in the Byzantine art that constitutes the subject of the present study. Given the general lack of literary sources on the tradition of Byzantine painting and the absence of previous investigation on the topic of mordant gilding on Byzantine icons and wall paintings, it is inevitable that research must rely on any available resource. Western European and Byzantine art, however, developed in parallel with a constant exchange of influences between them and, therefore, their technology is expected to present similarities.

As previously mentioned, there are many types of mordants that craftsmen used for the application of gold leaf on various materials, for example stone, glass, cloth, ceramic, metal etc. The present study will focus on the oil-based mordants alone.

An early medieval written source that deals with the use of oil-mordants for gilding on wood and masonry is the "*Lucca Manuscript*". It is a collection of recipes on the craft of painting believed to have originated in Northern Italy, where it was compiled at the end of the

eighth century. In a recipe titled “*on different ways of gilding*” one of the mordants described contains linseed oil, fused gum and saffron, all mixed together with water and boiled. A variant is also described where the additional ingredient of fir resin is included.<sup>1</sup>

In another medieval compilation, the “*Mappae Clavicula*”, which contains virtually all that is in the “*Lucca Manuscript*” plus many additional recipes, besides the above-mentioned recipe and its variant where an unspecified resin is used instead of fir resin, a third version with pine resin and without saffron is also quoted.<sup>2</sup> This compilation was transcribed in Northern France or contiguous areas of Germany and has been studied through the tenth-century “*Sélestat Manuscript*” and twelfth-century “*Phillips-Corning Manuscript*” copies.<sup>3</sup>

A more detailed document on the process of oil-mordant ornamental gilding for panels and wall paintings comes from *Cennino D’Andrea Cennini*, who was trained as a pupil of the Florentine painter Agnolo Gaddi at the turn of the fourteenth century. In chapter CLI of his treatise he gives a mordant recipe where linseed oil, which had been previously cooked on the fire or left in the sun, was ground with white lead, verdigris and varnish and then the whole mixture was boiled for a while and left to stand. Interestingly, Cennini remarks in the next chapter that in order to accelerate or delay the drying of this mordant the painter had to add a greater or lesser amount of verdigris respectively, while a little bole had to be also added in the first case.<sup>4</sup> *Giorgio Vasari*, a distinguished painter and architect from Arezzo,

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<sup>1</sup> *A Classical Technology Edited From the Codex Lucensis, 490*, edited by J.M. Burnam, The Gorham Press, Boston (1920), p. 119-120.

<sup>2</sup> *Mappae Clavicula - A Little Key to the World of Medieval Techniques*, edited by C.S. Smith and J.G. Hawthorne, Transactions of the American Philosophical Society, New Series, Vol. 64, Part 4, The American Philosophical Society, Philadelphia (1974), p. 43-44. The recipe 113-A of the “*M. C.*” does not exactly correspond to the 703 E of the “*Lucca*”, because of the difference in the quantity of gum used.

<sup>3</sup> *Ibidem*, p. 3-22.

<sup>4</sup> CENNINI, C., *The Craftsman's Handbook - The Italian 'Il Libro dell'Arte'*, translated by D.V. Thompson, Dover Publications, Inc., New York (1960), p. 58-59 & 96-97.

Tuscany, in the introduction of his treatise “*Vite degli Artisti*”, published in 1550 A.D., refers to the same type of mordant.<sup>5</sup>

At the end of the fourteenth century *Jehan Alcherius* (or Alcerius) started collecting and writing down various recipes on painting that a few years later would form part of a compilation of manuscripts gathered together by *Jehan Le Begue*. The “*Manuscripts of Jehan Le Begue*”, compiled in Paris in 1431 A.D., contain a recipe titled “*to make a mordant which will not be affected by the weather*” that Jehan Alcherius copied from a book lent to him by Giovanni da Modena, a painter living in Bologna. The mordant mixture described consists of linseed oil ground up with minium viz. red lead, ceruse viz. white lead, verdigris, ochre, bole and varnish, while the components of oil and gold size are also mentioned, although without giving any specific details.<sup>6</sup>

In the handbook the “*Strasburg Manuscript*” written in Germany in the fifteenth century, a detailed description is given on how to prepare and paint out an oil-mordant on wood and on the wall, as well as on how to lay gold leaf on top of it. According to this recipe, a mixture of linseed oil, red lead, ochre, Armenian bole, white calcined bone, zinc vitriol and varnish had to be made, all ingredients very well ground together and following a specific order. The procedure of applying the mordant and the gold leaf is exactly the same as that already described in the previous chapter of this study. A difference, however, is observed in the method of preparing a wooden surface for gilding; it is suggested that several coats of parchment size were first applied for the purpose of diminishing the absorbency of the wood.<sup>7</sup> This tip, however, does not apply to icons, as the mordant-gilded decoration was always executed above the paint layers. As far as wall paintings are concerned, the

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<sup>5</sup> *Vasari on Technique*, translated into English by L.S. Maclehorse & edited with introduction and notes by Prof. G. Baldwin Brown, Dover Publications, Inc., N. York (1960), p. 249-250 and VASARI, G., *Le Tecniche Artistiche*, introduzione e commento di G. Baldwin Brown, Neri Pozza Editore, Vicenza (1996), p. 232.

<sup>6</sup> *Manuscripts of Jehan Le Begue*, in MERRIFIELD, M.P., *Original Treatises on the Arts of Painting*, Vol. I, Dover Publications, New York (1967), p. 94.

<sup>7</sup> The same instructions are also given by G. Vasari (see note 5).

author of the manuscript recommends that the mordant should be laid over a layer of oil, presumably on top of the parchment size previously mentioned.<sup>8</sup>

In the sixth book of the "*Bolognese Manuscript*" that is composed of recipes on the decorative arts practised at Bologna in the fifteenth century, a mordant for gilding on walls is described. This could be produced by grinding together linseed oil, parchment glue, calcined bone, saffron and varnish. The anonymous author of this manual also gives some additional information; the mortar of the wall had to be dry before the process of gilding began, while the layer of the mordant should be not too thick and left to stand for five to six days before the gold leaf could be laid on.<sup>9</sup> Another mordant for gilding on wood, gesso, mortar and walls, amongst other materials, is included in the same section and made by grinding a mixture of linseed oil, litharge, verdigris, ochre and varnish.<sup>10</sup>

The "*Brussels Manuscript*", a treatise on the art of painting that was written by the painter *Pierre Le Brun* at Paris in 1635 A.D. includes a description of "*matte gold*" (i.e. unburnished) together with guidelines on how to obtain it. Amongst other things, the preparation of a mordant made of oil and dirty colours is explained. The oil was first boiled with the colours that the painter had already used, strained through a cloth and then boiled again. Ground pigments of yellow ochre, massicot and minium could also be added to the mixture. A variant made of linseed or walnut oil and Armenian bole is also mentioned. The alternative of leaving the mixtures to stand in the sun instead of boiling them is provided as well.<sup>11</sup>

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<sup>8</sup> *The Strasburg Manuscript: A Medieval Painters' Handbook*, translated from the old German by V.& R. Borradaile, A. Tiranti, London (1966), p. 61-63 & 65-67.

<sup>9</sup> *Bolognese Manuscript*, in MERRIFIELD, M.P., *Original Treatises on the Arts of Painting*, Vol. II, Dover Publications, New York (1967), p. 464.

<sup>10</sup> *Ibidem*, p. 472.

<sup>11</sup> *Brussels Manuscript*, in MERRIFIELD, M.P., *Original Treatises on the Arts of Painting*, Vol. II, Dover Publications, New York (1967), p. 836-838.

The recipe mentioned above that makes use of the dirty colours left on the painter's palette is also found in the handbook of *Felipe Nunes*, enriched with an additional varnish component.<sup>12</sup> Another mordant for application on wood made of "polimento", i.e. a mixture of pigment ground with oil or light, clear varnish, is also quoted in which light or dark ochre was used.<sup>13</sup> The artist and writer *Felipe Nunes* published this work titled "*Art of poetry and of painting and symmetry, with principles of perspective*" at Lisbon in 1615 A.D.

In the "*Manuscript De Mayerne*", a monograph that was written by the first physician of the court of England *Théodore Turquet De Mayerne* between 1620 and 1646 A.D., a slightly different mordant is described. This consists of oil, minium, yellow ochre and garlic, again ground and boiled together. In this case the gold leaf was laid over a completely dry mordant layer, the adhesion to it being achieved by the use of garlic (an explanation follows).<sup>14</sup> In another section of the same work the author states a variation of this recipe in which linseed oil, white lead, yellow ochre, umber, garlic and onion were used and processed in the same way.<sup>15</sup>

The last documentary source on painting to be quoted in this context and the only one compiled according to the Byzantine tradition is the so-called "*Hermeneia*", written by *Dionysius of Fournà* between 1730 and 1734 A.D. The recipe given for the preparation of an oil-mordant for use on walls and other materials is quite ambiguous, for some of the ingredients are referred to in contemporary workshop terms and the interpretation still remains obscure. The main component of this

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<sup>12</sup> *Artists' Techniques in Golden Age Spain: Six Treatises in Translation*, edited and translated by Z. Veliz, Cambridge University Press (1986), p. 6.

<sup>13</sup> Ibidem, p. 13-14.

<sup>14</sup> DE MAYERNE, THÉODORE TURQUET, *Pictoria, Sculptoria et Quae Subalternarum Artium* (1620), edited by M. Faidutti, C. Versini and published in *Peintures-Pigments-Vernis*, Audin, Lyon, August 1965, p. 519.

<sup>15</sup> Ibidem, July 1966, p. 572.



mordant is a substance called “peziri”;<sup>16</sup> the fact that this ingredient needed to be cooked first and from the context in which this term has been employed in other parts of the manual, it can be deduced that it refers to a drying oil, most probably linseed oil.<sup>17</sup> Two ambiguous pigments referred to as “psimythi” and “souligeni” along with verdigris, fine ochre and eggshells were ground and added to the oil. “Psimythi” is a white pigment and, again given the context of its frequent employment in other parts of the manual, implies it is either lime white or white lead, most probably white lead.<sup>18</sup> “Souligeni” is only mentioned by Dionysius once and accordingly remains uninterpreted.

Apart from the oil-based mordants that are cited by the various painting-theoreticians above, craftsmen were also using other general-purpose mordants whereby gold leaf was adhered to miscellaneous substrates, including wood and masonry. The most frequently encountered in the literature were the garlic-based mordants made of garlic juice mixed with various pigments such as white lead, red lead and bole, as well as other substances such as gum, vinegar and urine. The resultant liquid was a quick-drying mordant that could be gilded immediately or after it had dried by breathing on it to restore its tack. It is likely garlic mordants came into use in the late fourteenth century and have been described in a number of written sources.<sup>19, 20, 21, 22, 23</sup>

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<sup>16</sup> *The ‘Painter’s Manual’ of Dionysius of Fournā*, translated into English by P. Hetherington, Oakwood Publications (1996), p. 15 and ΔΙΟΝΥΣΙΟΥ ΤΟΥ ΕΚ ΦΟΥΡΝΑ, *Ερμηνεία της Ζωγραφικής Τέχνης*, υπό Α. Παπαδόπουλου-Κεραμέως, Εκδόσεις Κ.Χ. Σπανού, Πετρούπολη (1909), p. 42.

<sup>17</sup> *Ibidem*, p. 9 and p. 24 respectively.

<sup>18</sup> See *The ‘Painter’s Manual’ of Dionysius of Fournā*, translated into English by P. Hetherington, Oakwood Publications (1996), p. 92 (page 5, note 3) and SENDLER, E., *The Icon: Image of the Invisible*, translated by Fr. S. Bigham, Oakwood Publications (1988), p. 198.

<sup>19</sup> CENNINI, C., *The Craftsman’s Handbook - The Italian ‘Il Libro dell’Arte’*, translated by D.V. Thompson, Dover Publications, Inc., New York (1960), p. 97-98.

<sup>20</sup> *Manuscripts of Jehan Le Begue*, in MERRIFIELD, M.P., *Original Treatises on the Arts of Painting*, Vol. I, Dover Publications, New York (1967), p. 94.

<sup>21</sup> *Bolognese Manuscript*, in MERRIFIELD, M.P., *Original Treatises on the Arts of Painting*, Vol. II, Dover Publications, New York (1967), p. 468.

The use of other gold sizes containing ingredients like egg white, various gums, honey, pitch glue etc. is also encountered. As previously mentioned, *Plinius* first cites the use of egg white for use on materials that could not be heated in high temperatures (i.e. not metals).<sup>24</sup> *Theophilus Presbyter* in chapter twenty-three of his first book also describes the technique of applying gold leaf with egg white and states that this method could be used to ornament haloes, stoles and hems and that gold could also be similarly applied on walls.<sup>25</sup> Recipes for the preparation of other gold sizes can be found in the "*Mappae Clavicula*"<sup>26</sup> and in the "*Strasburg Manuscript*"<sup>27</sup>.

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<sup>22</sup> *Marciana Manuscript*, in MERRIFIELD, M.P., *Original Treatises on the Arts of Painting*, Vol. II, Dover Publications, New York (1967), p. 622-626.

<sup>23</sup> BOMFORD, D., DUNKERTON, J., GORDON, D., ROY, A., *Art in the Making: Italian painting before 1400: Exhibition Catalogue*, London, 29 November 1989 - 28 February 1990, National Gallery, London (1989), p. 46.

<sup>24</sup> PLINIUS C. SECONDUS, *Natural History* in Ten Volumes, with an English translation by H. Rackham, Volume IX, Libri XXXIII-XXXV, William Heinemann, London (1968), p. 51

<sup>25</sup> THEOPHILUS, P., *On Divers Art: The Treatise of Theophilus*, translated by J.G. Hawthorne and C.S. Smith, University of Chicago Press, Chicago (1963), p. 31.

<sup>26</sup> *Mappae Clavicula - A Little Key to the World of Medieval Techniques*, edited by C.S. Smith and J.G. Hawthorne, Transactions of the American Philosophical Society, New Series, Vol. 64, Part 4, The American Philosophical Society, Philadelphia (1974), p. 42.

<sup>27</sup> *The Strasburg Manuscript: A Medieval Painters' Handbook*, translated from the old German by V.& R. Borradaile, A. Tiranti, London (1966), p. 67.

## B. Secondary Sources

Following the attempt to trace and record the information gained from historical sources about the composition and application of oil-mordants on wood and on the wall, an investigation of the work published on this subject to date will be presented in this second section. The literature was searched for technical examinations of mordant gilding on panels, murals and polychrome sculptures. No publications were found describing any analyses of Byzantine paintings and this lack of information confirms the importance of this study. Therefore, as for primary sources, it is necessary to consider examples from Western European art. It should be noted that most of the results presented below were obtained by optical observations of the painted surfaces under the microscope and of cross sections of the samples by reflected visible light and ultra-violet radiation.

A relatively early article that deals with oil-mordant gilding concerns the results of the analysis of gold fragments derived from the vault of the first century B.C. *Aula Isiaca*", Palatino, Rome. The gold leaf was attached to the underlying clay-containing lime preparation by means of a very thin layer of varnish. The reaction of ammonia and hydrogen peroxide for detection of resins, oils and waxes proved positive. This was interpreted as the mordant most probably being an oil-based varnish.<sup>28</sup>

A scene from the wall paintings of the "Alte Kirche" in Wunstorf-Idensen, Lower Saxony, Germany dating from c.a. 1130 A.D. includes a decorative motif with traces of gilding. The thin gold leaf (1-2  $\mu\text{m}$ ) was applied to the substrate by a thin greyish preparation that consists of white lead, carbon black and a siccative oil medium. Pyrolysis-gas-chromatography confirmed a significant similarity to a laboratory

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<sup>28</sup> MARABELLI M., *Frammenti di Oro con Sottostante Preparazione, Prelevati dalla Volta (Aula Isiaca)*, Bolletino dell'Istituto Centrale del Restauro, Istituto Poligrafico dello Stato (1967), p. 55-56.

reference sample prepared with white lead-boiled linseed oil and aged for fifteen years.<sup>29</sup>

The Crucifix of the Hemse Church in Gotland, Sweden that dates from 1170-1190 A.D. shows gilded ornamentation on the cross, as well as on Christ's crown and loin-cloth. Some parts of the gilding are wrinkled in a way that is characteristic of oil. The gold leaf (0.2  $\mu\text{m}$ ) was applied on a mordant that formed a distinct light brownish-pink layer approximately 30  $\mu\text{m}$  thick, on top of the white oil-ground. The pigments contained in the mordant are white lead, some vermilion and organic red colouring material. The results of the analyses carried out by solubility tests, infrared spectroscopy and gas chromatography showed that the medium used is a drying oil, even though the presence of a resinous material cannot be ruled out.<sup>30</sup>

A second example of Romanesque gilded mural decoration are the wall paintings of the Holy Sepulchre Chapel in Winchester, England. The two samples that were taken from the gilded areas of the first painting scheme executed in 1175 A.D. were analysed by FT-IR (Fourier transform infrared spectroscopy), which indicated that a resinous mordant (20  $\mu\text{m}$ ) was used to adhere the gold leaf (5  $\mu\text{m}$ ).<sup>31</sup>

As will be shown, there are many examples of oil-mordant used for the gold outlines and ornamental motifs of late-medieval and early-Renaissance Italian panel paintings. For example, in a Crucifix painted by the *Master of St. Francis* in ca. 1272-1280 A.D., the folds of Christ's loin-cloth were adorned with gold applied over a raised dark red-brown

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<sup>29</sup> MATTEINI, M., MOLES, A., *Mural Paintings in Wunstorf-Idensen: Chemical Investigations on Paintings, Materials and Techniques*, Arbeitshefte zur Denkmalpflege in Niedersachsen, 11 (1994), p. 85.

<sup>30</sup> TÄNGEBERG, P., *The Crucifix from Hemse* and PLAHTER, U., *The Crucifix from Hemse: Analyses of the Painting Technique*, Maltechnik Restauro, 90 (1984), p. 28, 30 & 36.

<sup>31</sup> HOWARD, H.C., *Techniques of the Romanesque and Gothic Wall Paintings in the Holy Sepulchre Chapel, Winchester Cathedral*, in *Historical Painting Techniques, Materials and Studio Practice, Preprints of a Symposium, University of Leiden, the Netherlands, 26-29 June 1995*, edited by A. Wallert, E. Hermens, M. Peek, The Getty Conservation Institute (1995), p. 97.

oil-mordant layer ca. 40  $\mu\text{m}$  thick, which consists of carbon black, red lead and possibly verdigris as well (Plate 1).<sup>32</sup>

"*The Pentecost*" (1305-1317 A.D.), one of a series of six panels painted by Giotto, shows mordant-gilded decorative patterns mainly on the architecture of the scene. The flat, light grey-brown mordant (12-14  $\mu\text{m}$ ), which has been examined by staining tests with Sudan Black 10B and heating tests on the microscope hot-stage, was found to contain drying oil with a little pigment, principally white lead (Plate 2).<sup>33</sup>

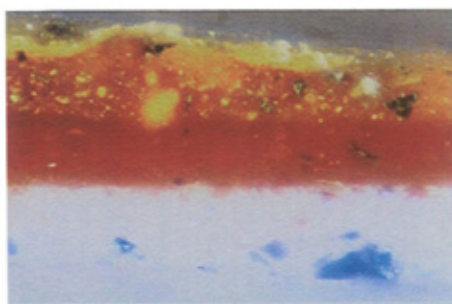


Plate 1 – *Crucifix* (350x)

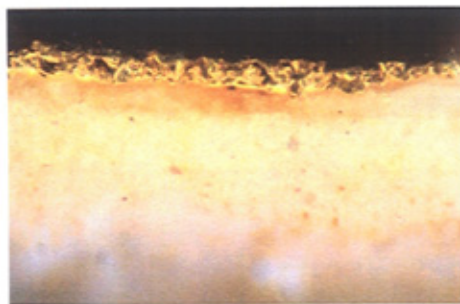


Plate 2 - *The Pentecost* (570x)

"*The Annunciation*", a panel that formed part of Duccio's "*Maestà*" altarpiece painted between 1308 and 1311 A.D., is a further example. Again, by using the staining and heating tests mentioned above, as well as X-radiographs, XRD (X-ray diffraction) and LMA (laser microspectral analysis) it was deduced that the raised fine gold outlines of the Virgin's blue cloak are composed of gold leaf (<1  $\mu\text{m}$ ) and a layer of mid-golden-brown mordant (maximum thickness 110  $\mu\text{m}$ ), which consists of lead white, yellow-brown ochre, a little red lead and possibly verdigris, all mixed in an oil medium (Plate 3).<sup>34</sup> The same striking raised mordant

<sup>32</sup> BOMFORD, D., DUNKERTON, J., GORDON, D., ROY, A., *Art in the Making: Italian painting before 1400: Exhibition Catalogue*, London, 29 November 1989 - 28 February 1990, National Gallery, London (1989), p. 47 & 63.

<sup>33</sup> Ibidem, p. 47 & 70.

<sup>34</sup> Ibidem, p. 47 & 82-83 and PLESTERS, J., ROY, A., BOMFORD, D., *Interpretation of the Magnified Image of Paint Surfaces and Samples in Terms of Condition and Appearance of the Picture*, in *Science and Technology in the Service of Conservation, Preprints of the Contributions to the Washington Congress, 3-9 September 1982*, edited by N.S. Brommelle and G. Thomson, IIC, London (1982), p. 171-172.

gilding is observed in *"The Transfiguration"*, another panel that belongs to the *"Maestà"* (Plate 4), as well as in the triptych *"The Virgin and Child with Saints"*, again by Duccio. The composition of the mordants in both cases is identical to that described above.<sup>35</sup>



Plate 3 - *The Annunciation* (180x)

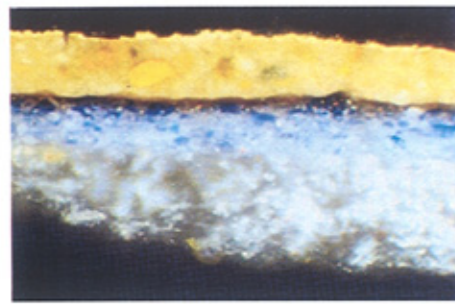


Plate 4 - *The Transfiguration* (130x)

The panels that belong to the *"Santa Croce"* altarpiece, painted by Ugolino di Nerio in ca. 1324-25 A.D., have also been mordant-gilded. Samples taken from two of them, the *"Sts. Andrew and Bartholomew"* and *"Two Angels"*, showed that the dark brown mordant layers (ca. 40  $\mu\text{m}$  and 25-30  $\mu\text{m}$  respectively) contain oil,<sup>36</sup> ochre and some verdigris, together with white and red lead, these last constituents being confirmed by XRD analysis (Plates 5 & 6).<sup>37</sup>

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<sup>35</sup> BOMFORD, D., DUNKERTON, J., GORDON, D., ROY, A., *Art in the Making: Italian painting before 1400: Exhibition Catalogue*, London, 29 November 1989 - 28 February 1990, National Gallery, London (1989), p. 47, 89 & 97.

<sup>36</sup> In the second panel the presence of drying oil was suggested again by the staining and heating tests previously mentioned.

<sup>37</sup> BOMFORD, D., DUNKERTON, J., GORDON, D., ROY, A., *Art in the Making: Italian painting before 1400: Exhibition Catalogue*, London, 29 November 1989 - 28 February 1990, National Gallery, London (1989), p. 47 & 113-114.



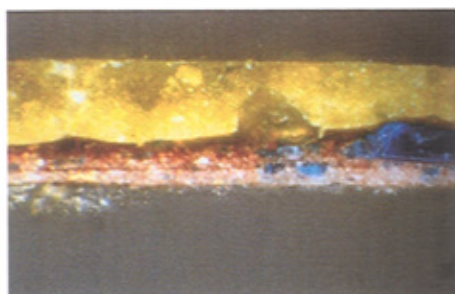


Plate 5 - Sts. Andrew and Bartholomew (130x)



Plate 6 - Two Angels (595x)

In an early Italian fresco representing "*Virgin and Child Enthroned with St. John the Baptist and St. Benedetto*", which was painted by Tommaso di Stefano or (also called Giotto) in 1356 A.D., the gilding was executed using a lamination technique. By observing the stratigraphy of some gilding samples under the microscope, the author discerned a yellow-brown mordant 90  $\mu\text{m}$  thick between the tin foil and the plaster, as well as an extremely thin film of mordant between the tin foil (ca. 25  $\mu\text{m}$ ) and the gold leaf (ca. 3  $\mu\text{m}$ ). Chemical microanalysis, infrared spectrophotometry and gas chromatography revealed the presence of linseed oil in the thick tin foil mordant and of a proteinaceous substance in the gold leaf mordant.<sup>38</sup>

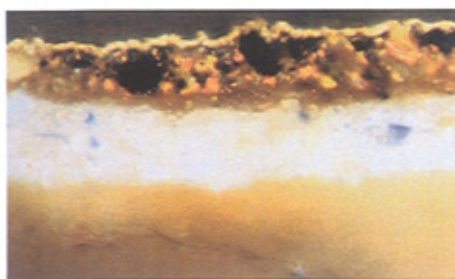


Plate 7 - Three Saints (490x)

Nardo di Cione painted the altarpiece "*Three Saints: St. John the Baptist with St. John the Evangelist (?) and St. James*" that was commissioned in ca. 1365 A.D. A sample of the flat, mid-brown mordant layer (maximum thickness 20  $\mu\text{m}$ ) was taken from the gold border of St. John the Evangelist's green cloak.

<sup>38</sup> MATTEINI, M., MOLES, A., Tommaso di Stefano detto Giotto - *Madonna col Bambino in Trono fra San Giovanni Battista e San Benedetto con Otto Angeli*, in *Metodo e Scienza Operatività e Ricerca nel Restauro, Catalogo della mostra, Firenze, 23 giugno 1982 - 6 gennaio 1983*, a cura di U. Baldini, Sansoni Editore, Firenze (1982), p. 91-92.

It was found to contain both lead and iron, presumably as white lead or lead oxide, as well as a mixture of yellow and red ochres and bone black, however, the sample was too small to test for the medium (Plate 7).<sup>39, 40</sup>

Lorenzo Monaco's panel the "Coronation of the Virgin" also dates from the fourteenth century. Mordant-gilded patterns have been applied along the sleeve and hem edges and in rosettes on the front of the Virgin's robe by means of a mordant that contains white lead.<sup>41</sup>

Another altarpiece called "The San Pier Maggiore" that was painted by Jacopo di Cione in 1370-1371 A.D. was also examined. In some areas the barely raised red-brown mordant was as thin as 10 µm and consequently it was not easily discernible or measurable. Two samples that were taken from where the mordant layer is 40-50 µm and 20-40 µm thick, were found to be rich in medium, presumably oil, and to contain red iron oxide, i.e. a granular red-brown earth, as well as some lead white (Plates 8 & 9).<sup>42</sup>

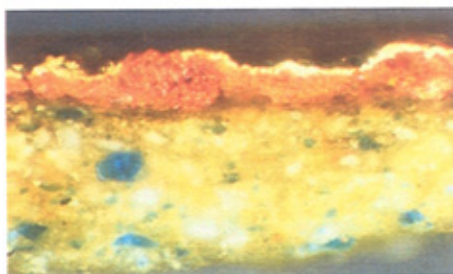


Plate 8 - The San Pier Maggiore  
(130x)

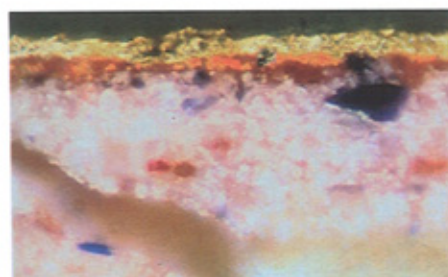


Plate 9 - The San Pier Maggiore  
(490x)

<sup>39</sup> BOMFORD, D., DUNKERTON, J., GORDON, D., ROY, A., *Art in the Making: Italian painting before 1400: Exhibition Catalogue*, London, 29 November 1989 - 28 February 1990, National Gallery, London (1989), p. 47 & 137-138.

<sup>40</sup> PLESTERS, J., ROY, A., *The Materials and Technique: Cennino Cennini's Treatise Illustrated*, National Gallery Technical Bulletin, 9 (1985), p. 33.

<sup>41</sup> BURNSTOCK, A., *The Fading of the Virgin's Robe in Lorenzo Monaco's Coronation of the Virgin*, National Gallery Technical Bulletin, 12 (1988), p. 58.

<sup>42</sup> BOMFORD, D., DUNKERTON, J., GORDON, D., ROY, A., *Art in the Making: Italian painting before 1400: Exhibition Catalogue*, London, 29 November 1989 - 28 February 1990, National Gallery, London (1989), p. 47 & 182.



Three different samples of gilding from the wall paintings of the Palazzo della Ragione in Padua that are attributed to *Giusto de Menabuoi* (1320/30-1397 A.D.), were investigated by GC/MS (gas chromatography/mass spectrometry). In the first sample, which is believed to belong to the original Menabuoi decoration, the preparation layer of the gold leaf is reported to mainly consist of a mixture of Venice turpentine and pinaceae resins.<sup>43</sup>

During the restoration of the early fifteen-century stuccoes that decorate the Old Sacristy of the Church of St. Lorenzo in Florence, it was revealed that *Donatello* used a lamination technique to execute the gilding decoration. Under ultra-violet radiation the two oil-mordant layers of the successive metallic sheets of tin (10-15 µm) and gold (2-3 µm) fluoresce strongly. However, the colour of fluorescence of the mordant between the gold leaf and the tin foil (10-15 µm) appears to be slightly more orange than the mordant between the tin foil and the plaster (40-50 µm), which the authors attribute to the possible presence of a resinous substance.<sup>44</sup>

An early fifteenth-century wall painting depicting “*St. Michael Weighing Souls*” from the choir of the Real Convento de Santa Clara in Toledo was examined by Véliz *et al.* The mordant consists of a mixture of white and red lead, umber black and traces of vermilion with a high proportion of medium, most probably oil.<sup>45</sup>

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<sup>43</sup> FEDRIGO, M.A., FAVARO, M., TRALDI, P., *Applications of Mass Spectrometry in Cultural Heritage: Identification of Ligands Employed for Mordant Gilding*, *Rapid Communications in Mass Spectrometry*, 14 (2000), p. 2203-2209.

<sup>44</sup> MATTEINI, M., MOLES, A., *Studi Analitici, Chimici e Stratigrafici dei Materiali e delle Strutture Pittoriche*, in *Donatello e La Sagrestia Vecchia di San Lorenzo: Temi, Studi, Proposte di un Cantiere di Restauro*, Firenze, *Sagrestia Vecchia della Basilica di San Lorenzo*, 20 giugno - 13 settembre 1986, Centro Di, Firenze (1986), p. 67-68 and the same text translated in English: *Analytical, Chemical and Stratigraphic Studies of the Painting Layers and Materials*, *The Burlington Magazine*, 129 (1987) p. 43.

<sup>45</sup> VÉLIZ, Z., BABINGTON, C., GONZÁLEZ, M.C., ILLÁN, A., *Technique and Treatment of the St Michael Weighing Souls in the Royal Convent of Santa Clara, Toledo, Spain*, in *Conservation of the Iberian and Latin American Cultural Heritage, Preprints of the Contributions to the Madrid Congress, 9-12 September 1992*, edited by H.W.M. Hodges, J. S. Mills, P. Smith, IIC, London (1992), p. 169 & 171-172.

The polychromed sculptures of the high shrine altar from the church of St. James in Rothenburg, Germany are attributed to *Friedrich Herlin* and were completed in 1466 A.D. A sample from a mordant-gilded area was examined by micro-chemical analysis and thin-layer chromatography and showed a ca. 40 µm thick layer of mordant containing red lead and ochre in a possibly resinous medium.<sup>46</sup> Another high altar painted by Herlin in 1474 A.D. is kept in the church of St. Blase in Bopfingen, Southern Germany. Samples taken from the mordant gilding of the two interior scenes of the altar wings showed that the mordant is composed of a drying oil and a little white lead.<sup>47</sup>

One of the earliest attempts to analyse gilding fragments from wall paintings dates from the late eighteenth century and appears in Merrifield. Professor Branchi from Pisa conducted experiments on gilding samples taken from the wall paintings of the Campo Santo at Pisa that *Benozzo Gozzoli* and *Buonamico Buffalmacco* painted between 1468 and 1484 A.D. After carrying out various tests, he concluded that the gold leaf was laid upon a thin coating of wax, which was in turn applied on a yellow "size" painted directly onto the wall plaster. He also reported that the wax used by Benozzo Gozzoli must have been dissolved either in a volatile or, more likely, a fixed drying-oil. No such indication has been reported for Buffalmacco's wall paintings.<sup>48</sup>

During the restoration of *Domenico Ghirlandaio's* frescoes in the church of Santa Maria Novella at Florence (painted in 1485-1490 A.D.), gilding samples were observed under the microscope. It was revealed that Ghirlandaio had also used a lamination technique for the gilded embellishments. Both the tin and the gold mordants fluoresce in ultra-violet radiation, but each one of them with different colour, an intense

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<sup>46</sup> BROEKMAN-BOKSTIJN, M., VAN ASPEREN DE BOER, J.R.J., VAN' T HUL-EHRNREICH, E.H., VERDUYN-GROEN, C.M., *The Scientific Examination of the Polychromed Sculpture in the Herlin Altarpiece*, *Studies in Conservation*, 15 (1970), p. 380-381.

<sup>47</sup> RIEBER, F., STRAUB, R.E., *The Herlin altarpiece at Bopfingen (1474): Technique and Condition of the Painted Wings*, *Studies in Conservation*, 22 (1977), p. 143.

<sup>48</sup> MERRIFIELD, M.P., *Original Treatises on the Arts of Painting*, Vol. I, Dover Publications, New York (1967), p. xcv-xcviii.

light yellow for the former and orange for the latter. Bandini *et al.* interpret this florescence as the presence of proteinaceous substances and drying oil in both, perhaps glue in emulsion with oil, as well as the possible existence of a further component in the gold mordant, probably resin.<sup>49</sup>

The mordant gilding ornamentation of three late fifteenth-century Florentine panels that were painted by Domenico Ghirlandaio, his brother David Ghirlandaio and an imitator of *Fra Filippo Lippi* respectively was examined by Dunkerton *et al.* They report that in the first two cases the mordant layers are identical and both contain lead white and brown earth in a high proportion of medium, while in the Lippi the mordant is composed of vegetable black, vermilion and red earth.<sup>50</sup>

Mordant gilding was also used in Northern European painting and, in particular, in the applied relief gilding of the Netherlandish and German paintings of 1400-1550 A.D. In Cranach's "*Saints Genevieve and Apollonia*" and in *The Master of the Life of the Virgin's* "*The Presentation in the Temple*" (ca. 1460-1475 A.D.) the brownish-yellow medium-rich mordant was found to contain lead white, some lead-tin yellow, a yellow earth and a little red earth in linseed oil. In the mordant-gilded areas of the four "*Werden Altarpiece*" panels from the workshop of *The Master of the Life of the Virgin* the same researcher found that the composition of the mordant is rather similar, with small quantities of lead white, lead-tin yellow, yellow earth, a little black and azurite in linseed oil. In one of those, "*The Conversion of Saint Hubert*" (ca. 1480-85 A.D.), the linseed oil present in the mordant that was used for the gilded applied relief brocade was found to have been heat-bodied. The mordants of the

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<sup>49</sup> BANDINI, F., BOTTICELLI, G., DANTI, C., MATTEINI, M., MOLES, A., *The Restoration of Domenico Ghirlandaio's Frescoes in the Cappella Maggiore of the S. Maria Novella in Florence: Problems, Practical Work, Results*, in *Case Studies in the Conservation of Stone and Wall Paintings, Preprints of the Contributions to the Bologna Congress, 21-26 September 1986*, edited by N.S. Brommelle and P. Smith, IIC, London (1986), p. 186-187.

<sup>50</sup> DUNKERTON, J., ROY, A., *The Materials of a Group of Late Fifteenth-Century Florentine Panel Paintings*, National Gallery Technical Bulletin, 17 (1996), p. 27 & 30.

panels painted by *The Master of Liesborn* and his circle consist of much the same mixture, with the addition of a little red lake. The mordants used by the Cologne painter *The Master of the Saint Bartholomew Altarpiece* are pale yellow and quite opaque, consisting of lead white and yellow earth.<sup>51</sup>

Stuccoes in the church of San Ambrogio at Cantù, Como, Italy that date from the baroque period have been enriched with ornamental gilding. Toniolo *et al.*, using gas chromatographic/mass spectrometric analysis, revealed that the gold leaf (up to 5 µm thick) was attached to the surface of the stuccoes by using an orange-red linseed-oil-based mordant composed of litharge, which acted as a drier and/or inert pigment, red lead and possibly some red ochre.<sup>52</sup>

Lastly, the baroque “*Altar of Santo Antônio*” of the Mother Church of Our Lady of Conception in Catas Altas, Minas Gerais, Brasil became the subject of a study due to its Asian-style painted motifs. Samples taken from matte gilded decorations and painted layers over the gold and examined by SEM-EDX (scanning electron microscopy/energy-dispersive X-ray) analysis revealed that the mordant layer contains lead-containing particles, together with clay and iron oxides.<sup>53</sup>

It is of interest to note the observation made by several of the researchers of the above works: in a number of panel paintings the presence of a thin layer of what appears to be pure unpigmented medium at the interface between the mordant and the paint layer was noted. Provided that an oil-resinous mordant was employed, this was

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<sup>51</sup> *Methods and Materials of Northern European Painting in the National Gallery, 1440-1550*, National Gallery Technical Bulletin, 18 (1997), p. 31-32.

<sup>52</sup> TONIOLO, L., COLOMBO, C., BRUNI, S., FERMO, P., CASOLI, A., PALLA, G., BIANCHI, C.L., *Gilded Stuccoes of the Italian Baroque*, Studies in Conservation, 43 (1998), p. 203-206.

<sup>53</sup> SOUZA, L.A.C., AVILA, C., *Chinese Motifs in the Baroque Art of Minas Gerais, Brasil: Historical and Technical Aspects*, in *Painted Wood: History and Conservation, Proceedings of a Symposium Organised by the Wooden Artifacts Group of the AIC, Williamsburg, Virginia 11-14 November 1994*, edited by V. Dorge and F.C. Howlett, The Getty Conservation Institute, Los Angeles (1998), p. 212-214.

attributed by the researchers either to the tendency of the oil and the varnish medium to separate or to the application of a colourless oil or varnish layer beneath the mordant.<sup>54, 55</sup>

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<sup>54</sup> BOMFORD, D., DUNKERTON, J., GORDON, D., ROY, A., *Art in the Making: Italian painting before 1400: Exhibition Catalogue*, London, 29 November 1989 - 28 February 1990, National Gallery, London (1989), p. 46.

<sup>55</sup> *Methods and Materials of Northern European Painting in the National Gallery, 1440-1550*, National Gallery Technical Bulletin, 18 (1997), p. 32, plate 12.

**CHEMISTRY OF DRYING OILS**

## A. Processing, Composition and Properties

As the main component of oil-mordants is a drying oil, predominantly linseed oil, a brief introduction to the nature and chemistry of drying oils follows. This chapter aims to offer the reader a better understanding of the role of oil in mordants.

Drying oils belong to the group of natural products known as *oils and fats*, which in turn form the major subgroup of a larger class known as *lipids*. Oils and fats occur naturally in both the animal and vegetable kingdoms, and have largely the same chemical structure, namely glycerol esters of fatty acids. The essential difference between them is that oils are usually liquid at room temperature, while fats are semi-solid or solid. Oils and fats form an important part of the normal human diet and have also been used since antiquity as sources of heat and illumination as well as for medical, cosmetic and other purposes.<sup>1, 2</sup>

Vegetable oils were originally extracted from crushed seeds or plant material by various methods all involving the use of leverage to compress bags of seeds to extract the oil. Any extraneous material or so-called “foots” in the extracted “raw oil”, such as protein or mucilage, was removed by washing with water or by settling after long storage. Further refining treatments, like that of bleaching in sunlight or heating in pots often made of lead, were also used to obtain a clearer oil characterised by its modified properties.<sup>3</sup>

Erhardt gives a brief history of oil processing for use in painting. The first references of oil extraction from the compression of seeds under high temperature appeared in the eighteenth century. This method led

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<sup>1</sup> GUNSTONE, F.D., HERSLÖF, B.G., *A Lipid Glossary*, The Oily Press, Dundee (1992), p. 33 & 53.

<sup>2</sup> FRANKEL, E.N., *Lipid Oxidation*, The Oily Press, Dundee (1998), p. 1.

<sup>3</sup> ERHARDT, D., *Paints Based on Drying-Oil Media*, in *Painted Wood: History and Conservation, Proceedings of a Symposium Organised by the Wooden Artifacts Group of the AIC, Williamsburg, Virginia 11-14 November 1994*, edited by V. Dorge and F.C. Howlett, The Getty Conservation Institute, Los Angeles (1998), p. 17-19.

to a considerable rise in oil yield and at the same time facilitated the removal of more extraneous material from the seeds. With the introduction of hydraulic presses in the late-eighteenth century, however, heating prior to or during oil processing became more common. The solvent extraction method was first proposed in the 1840s and became more practical in the twentieth century when a range of cheaper and more highly refined solvents became available. Acid and alkali refining methods were introduced in 1792 and 1923 respectively. These involve treatment of the oil with sulphuric acid in the first case and caustic soda or sodium carbonate in the second and lead to changes in its chemical properties. Currently, all oil is isolated from heated seeds using a pressure method (usually an expeller) or a solvent extraction process, followed by alkali refining to remove impurities or so-called “break”, such as free fatty acids, phosphatides and carbohydrates. Carlyle also presents an outline of the methods employed in extraction and clarification of oils for use in oil painting in Britain between 1800-1900 A.D. <sup>4</sup>

Vegetable oils can be classified into three groups according to their film-forming properties: the drying (e.g. linseed oil, walnut oil, poppy-seed oil, tung oil, perilla oil etc.), semi-drying (e.g. soya bean oil, safflower oil, tall oil etc.), and the non-drying oils (e.g. olive oil, castor oil, coconut oil etc.). The characteristic that distinguishes the drying oils from the rest is their natural ability to “dry”, by forming a semi-solid, elastic, and transparent film. <sup>5</sup> This important property has been known for well over a thousand years and their earliest application seems to have been that of coatings. Since the Middle Ages, however, drying oils have been used in painting as binding media for pigments, vehicles for

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<sup>4</sup> CARLYLE, L.A., *The Artist's Assistant - Oil Painting Instruction Manuals and Handbooks in Britain 1800-1900 - With Reference to Selected Eighteenth-century Sources*, Archetype Publications (2001), p. 31-40.

<sup>5</sup> *Encyclopedia of Polymer Science and Engineering*, Vol. 5, John Wiley & Sons (1986), p. 205.



varnishes, and adhesives for mordants. <sup>6</sup> Since the 19<sup>th</sup> century they have been chiefly used in the surface coatings and allied industries as vehicles for paints, <sup>7</sup> varnishes, and printing inks. Today, though, they have been almost completely replaced by other film-forming materials. <sup>8</sup>

Drying oils, like all oils and fats, are esters of trihydric alcohol or glycerol (also called glycerine) with three fatty acid molecules, hence the name *triglyceride* (alternatively called glycerol tri-ester or triacylglycerol). The equation shown in Figure 1 <sup>9</sup> is generally known as *esterification* and in this case results in the formation of a triglyceride. <sup>10</sup>

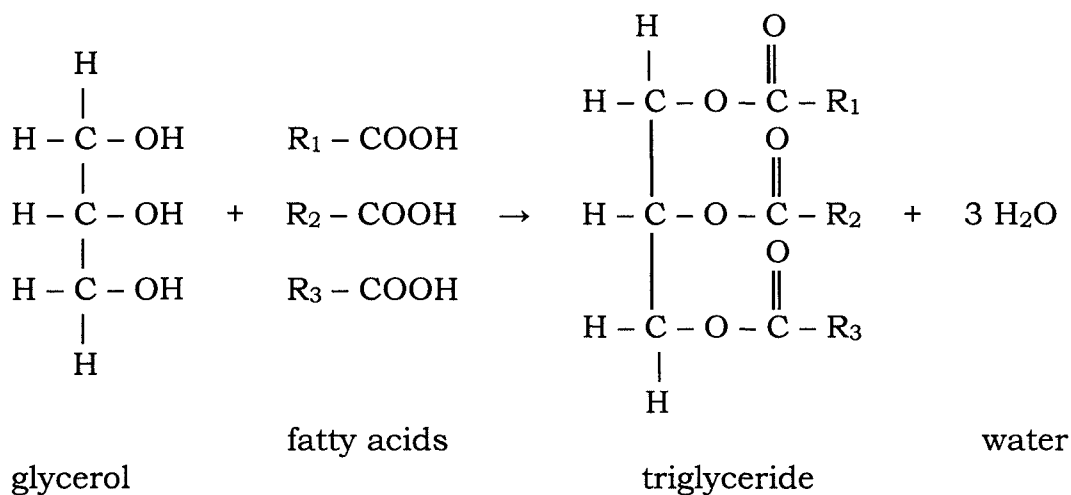


FIGURE 1

R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> represent alkyl or alkenyl groups varying in length and number of double bonds. Drying oils also contain small amounts of

<sup>6</sup> See ERHARDT, D., *Paints Based on Drying-Oil Media*, in *Painted Wood: History and Conservation, Proceedings of a Symposium Organised by the Wooden Artifacts Group of the AIC, Williamsburg, Virginia 11-14 November 1994*, edited by V. Dorge and F.C. Howlett, The Getty Conservation Institute, Los Angeles (1998), p. 17.

<sup>7</sup> MOSCA, M.J., *On Linseed Oil and Other Drying Oils Used in Paint Making*, *Traditional Paint News*, 1 (1996), p. 30-34.

<sup>8</sup> *Encyclopedia of Polymer Science and Engineering*, Vol. 5, John Wiley & Sons (1986), p. 203.

<sup>9</sup> Taken from WINGROVE, A.S., CARET, R.L., *Organic Chemistry*, Harper & Row Publishers, New York (1981), p. 1090.

<sup>10</sup> The reverse reaction whereby the ester is broken down to the components glycerol and fatty acids is called *hydrolysis*. See GUNSTONE, F.D., HERSLÖF, B.G., *A Lipid Glossary*, The Oily Press, Dundee (1992), p. 31& 43.

mono- and di-glycerides, in which glycerol has combined with one or two fatty acids, as well as free fatty acids and other organic compounds called *non-saponifiables*,<sup>11</sup> such as phosphatides, carbohydrates, sterols, colouring matter and water.

The properties of a triglyceride are determined by the specific combination of fatty acids it contains and, in turn, the properties of a drying oil are dependant upon the combination of the triglycerides it is composed of. Therefore the composition of drying oils is affected by variations of the plant species,<sup>12, 13, 14</sup> the nature of the soil, the season of harvesting<sup>15</sup> and the climatic conditions in which those plants were grown<sup>16</sup>. Furthermore, various methods of pressing, processing and refining of the individual drying oils result in differences in the physical, chemical, mechanical and optical properties of the resulting dried-oil films.<sup>17</sup>

The principal fatty acids encountered in drying oil triglycerides are straight-chain hydrocarbon saturated and unsaturated acids with an even number of carbon atoms that ranges between twelve and eighteen (eighteen being the most common) and with one to three double bonds for the unsaturated acids. Most unsaturated fatty acids have the first

<sup>11</sup> LERCKER, G., FREGA, N., CONTE, L.S., CAPELLA, P., *La Gascromatografia su Colonne Capillari (HRGC) nello Studio dell' Insaponificabile degli Olii Vegetali*, Rivista Italiana delle Sostanze Grasse, 58 (1981), p. 324-330.

<sup>12</sup> MCGREGOR, W.G., CARSON, R.B., *Fatty Acid Composition of Flax Varieties*, Canadian Journal of Plant Science, 41 (1961), p. 814-817.

<sup>13</sup> YERMANOS, D.M., *Variability in Seed Oil Composition of 43 Linum Species*, Journal of the American Oil Chemists' Society, 43 (1966), p. 546-549.

<sup>14</sup> SEKHON, K.S., GILL, K.S., AHUJA, K.L., SANDHU, R.S., *Fatty Acid Composition and Correlation Studies in Linseed (Linum Usitatissimum L.)*, Oléagineux, 28 (1973), p. 525-526.

<sup>15</sup> FORCHIERI, H., BERTONI, M.H., KARMAN DE SUTTON, G., CATTANEO, P., *Aceites de Semilla de Lino Oleaginoso. Composicion Quimica: Influencia de la Epoca de Siembra*, Anales de la Asociacion Quimica de Argentina, 53 (1970), p. 313-327.

<sup>16</sup> PRICE, M.J., *Comparative Fatty Acid Composition of Linseed Oil in Northern and Southern Queensland*, Queensland Journal of Agricultural and Animal Sciences, 25 (1968), p. 129-133.

<sup>17</sup> ERHARDT, D., *Paints Based on Drying-Oil Media*, in *Painted Wood: History and Conservation, Proceedings of a Symposium Organised by the Wooden Artifacts Group of the AIC, Williamsburg, Virginia 11-14 November 1994*, edited by V. Dorge and F.C. Howlett, The Getty Conservation Institute, Los Angeles (1998), p. 19 & 27-28.

double bond at carbon 9 (C<sub>9</sub>) with succeeding double bonds at carbons 12 and 15 (C<sub>12</sub> and C<sub>15</sub> respectively). The increase of unsaturation and decrease of the chain length of fatty acids lowers their melting point and for this reason the liquid vegetable oils are generally more unsaturated and/or contain larger proportions of shorter fatty acids than the solid animal fats.<sup>18</sup> The unsaturated linoleic and linolenic acids with two and three double bonds respectively are the compounds principally responsible for the drying properties of drying oils.<sup>19</sup> The names and formulas of the most common fatty acids are shown in Table 1.<sup>20</sup>

TABLE 1 – Common Fatty Acids

Name	No. of carbon atoms	No. of double bonds	Formula
Lauric	12	–	HOOC.(CH <sub>2</sub> ) <sub>10</sub> .CH <sub>3</sub>
Mystic	14	–	HOOC.(CH <sub>2</sub> ) <sub>12</sub> .CH <sub>3</sub>
Palmitic	16	–	HOOC.(CH <sub>2</sub> ) <sub>14</sub> .CH <sub>3</sub>
Stearic	18	–	HOOC.(CH <sub>2</sub> ) <sub>16</sub> .CH <sub>3</sub>
Oleic	18	1	HOOC.(CH <sub>2</sub> ) <sub>7</sub> .CH=CH-(CH <sub>2</sub> ) <sub>7</sub> -CH <sub>3</sub>
Linoleic	18	2	HOOC.(CH <sub>2</sub> ) <sub>7</sub> .CH=CH-CH <sub>2</sub> -CH=CH-(CH <sub>2</sub> ) <sub>4</sub> -CH <sub>3</sub>
Linolenic	18	3	HOOC.(CH <sub>2</sub> ) <sub>7</sub> .CH=CHCH <sub>2</sub> CH=CHCH <sub>2</sub> CH=CHCH <sub>2</sub> CH <sub>3</sub>

Several theories have been developed in order to predict the way in which fatty acids are distributed between the various triglyceride molecules, such as the principle of even distribution by Hilditch, the random theory by Dutton *et al.* and the restricted random theory of

<sup>18</sup> ERHARDT, D., *Paints Based on Drying-Oil Media*, in *Painted Wood: History and Conservation, Proceedings of a Symposium Organised by the Wooden Artifacts Group of the AIC, Williamsburg, Virginia 11-14 November 1994*, edited by V. Dorge and F.C. Howlett, The Getty Conservation Institute, Los Angeles (1998), p. 20-21.

<sup>19</sup> MILLS, J.S., WHITE, R., *The Organic Chemistry of Museum Objects*, Butterworth-Heinemann, 2<sup>nd</sup> Edition, Oxford (1999), p. 32.

<sup>20</sup> Taken from MILLS, J.S., *The Gas Chromatographic Examination of Paint Media: Part I. Fatty Acid Composition and Identification of Dried Oil Films*, *Studies in Conservation*, 11 (1966), p. 93.

Kartha.<sup>21, 22</sup> According to the theory by Gunstone, the central (secondary) hydroxyl group of all the glycerol molecules is preferentially esterified by a C<sub>18</sub> unsaturated acid, while the two primary hydroxyl groups are esterified in random manner by the saturated and any remaining unsaturated acids.<sup>23</sup> That means that the three main drying oils, which contain more than 80% unsaturated C<sub>18</sub> acids,<sup>24</sup> will contain one and the majority of them at least two molecules of unsaturated acids. In the case of linseed oil, however, a further amended theory has been presented that does not agree with that developed by Gustone.<sup>25, 26</sup>

The properties of drying oils are usually described by listing certain physical and chemical characteristics: colour, specific gravity, density, viscosity and refractive index<sup>27</sup> are physical properties, while the iodine number is an indicator of the degree of unsaturation<sup>28</sup>. Furthermore, acid value, saponification value and unsaponifiable matter are indicative of the acidic properties of a drying oil.<sup>29</sup> Other values that are used to characterise drying-oil molecules include peroxide value, hydroxy value and acetyl value.<sup>30</sup>

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<sup>21</sup> SONNTAG, N.O.V., *Structure and Composition of Fats and Oils in Bailey's Industrial Oil and Fat Products*, edited by D. Swern, Vol. 1, John Wiley & Sons, 4<sup>th</sup> Edition, N. York (1979), p. 1-98.

<sup>22</sup> *The Science of Surface Coatings*, edited by H.W. Chatfield, Ernest Benn Ltd, London (1962), p. 39-40.

<sup>23</sup> GUNSTONE, F.D., *Distribution of Fatty Acids in Natural Glycerides of Vegetable Origin*, Chemistry and Industry (1962), p. 1214-1223.

<sup>24</sup> See Table 2.

<sup>25</sup> VERESHCHAGIN, A.G., NOVITSKAYA, G.A., *The Triglyceride Composition of Linseed Oil*, Journal of the American Oil Chemists Society, 42 (1965), p. 970-974.

<sup>26</sup> MILLS, J.S., WHITE, R., *The Organic Chemistry of Museum Objects*, Butterworth-Heinemann, 2<sup>nd</sup> Edition, Oxford (1999), p. 32-33.

<sup>27</sup> See FAUVE, M., PONJEAN, C., *L'Indice de Réfraction, Son Utilisation Dans l' Étude des Huiles Siccatives*, FATIPEC Congres, 6 (1962), p. 203-208.

<sup>28</sup> See GUNSTONE, F.D., HERSLÖF, B.G., *A Lipid Glossary*, The Oily Press, Dundee (1992), p. 46.

<sup>29</sup> Ibidem, p. 2, 81 & 96.

<sup>30</sup> Ibidem, p. 1, 44 & 69.

Of all the drying oils, three have found most use in European painting, namely linseed, walnut and poppy-seed oil. Their fatty acid composition is shown in Table 2.<sup>31</sup> Linseed oil is pressed from the seed of the flax plant *Linum usitatissimum* that is grown in many parts of the world and has a deep yellow or brownish colour.<sup>32</sup> It was the more frequently used, probably because it dries more quickly than the other two and forms a hard durable film. Its main disadvantage, however, is that it yellows more when compared to walnut and poppy-seed oils.<sup>33</sup>

TABLE 2 - Fatty Acid Composition of Drying Oils (%)

	Linseed	Walnut	Poppyseed
Palmitic	6	8	10
Stearic	4	3	2
Oleic	22	15	11
Linoleic	15	61	76
Linolenic	52	12	–

As previously mentioned, the chief property that renders drying oils suitable materials for the preparation of mordants is their ability to dry when laid out in a thin film. The mechanism of film formation and degradation of drying oils is briefly presented in the following section.

<sup>31</sup> Taken from MILLS, J.S., *The Gas Chromatographic Examination of Paint Media: Part I. Fatty Acid Composition and Identification of Dried Oil Films*, Studies in Conservation, 11 (1966), p. 93.

<sup>32</sup> *Encyclopedia of Polymer Science and Engineering*, Vol. 5, John Wiley & Sons (1986), p. 204.

<sup>33</sup> MILLS, J.S., WHITE, R., *The Organic Chemistry of Museum Objects*, Butterworth-Heinemann, 2<sup>nd</sup> Edition, Oxford (1999), p. 36 & 40.

## B. Drying Process and Ageing

As drying oils are mixtures of compounds, the phenomenon of film formation under ambient conditions as a result of drying cannot be explained in terms of a simple uniform reaction scheme. Nevertheless, the process of drying and plasticisation can be ascribed to chemical changes such as oxidation, polymerisation and hydrolysis.<sup>34</sup>

Erhardt explains that the primary areas of reaction in a drying oil are the double bonds of the triglyceride fatty acids and the ester linkages. The double bonds undergo a number of reactions that result in the formation of bonds between the molecules, a process known as *cross-linking*. The drying oil is thus converted from a liquid first to a soft gel and then to a rubbery solid. The breakage of ester linkages is generally slow and leads to the eventual degradation of the dried-oil film, a subject that will be discussed further below.

A summary of the main reactions that constitute the drying process of oils, as presented by Mills & White, is given below.<sup>35, 36</sup> When a drying oil is spread out in a thin film, oxidative polymerisation of the poly-unsaturated fatty acids, namely the linoleic and linolenic acids (Table 1), begins to occur. This is due to the low energy that is required for the hydrogen atoms situated on the methylene group between two *un-conjugated* double bonds to break their bonds with their carbon

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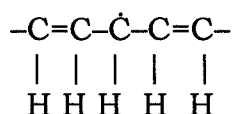
<sup>34</sup> ERHARDT, D., *Paints Based on Drying-Oil Media*, in *Painted Wood: History and Conservation, Proceedings of a Symposium Organised by the Wooden Artifacts Group of the AIC, Williamsburg, Virginia 11-14 November 1994*, edited by V. Dorge and F.C. Howlett, The Getty Conservation Institute, Los Angeles (1998), p. 21-24.

<sup>35</sup> MILLS, J.S., WHITE, R., *The Organic Chemistry of Museum Objects*, Butterworth-Heinemann, 2<sup>nd</sup> Edition, Oxford (1999), p. 36-38.

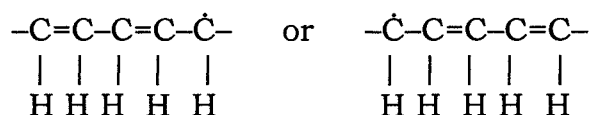
<sup>36</sup> MILLS, J.S., *The Gas Chromatographic Examination of Paint Media: Part I. Fatty Acid Composition and Identification of Dried Oil Films*, *Studies in Conservation*, 11 (1966), p. 92-108.

atoms.<sup>37</sup> Hence, the fatty acids in question begin to combine with oxygen in the air to form peroxides and with each other to form a 3-dimensional polymeric network. This phase of development of the oil film is called the *curing stage*.<sup>38</sup>

According to Mills & White, the first step in the drying process is the creation of a free radical by the removal of a hydrogen atom from a doubly *activated* position of an unsaturated acid, namely the position between two double bonds ( $-\dot{\text{C}}-$ )<sup>39</sup>:



A rearrangement of the position of the free radical, or isomerisation, occurs that leads to the creation of conjugated double bonds:



Some dissolved oxygen is always present in the wet oil film and is polarised and, therefore, active. The oxygen attacks the radical of the conjugated dienes resulting in the formation of *peroxides*. This reaction can take place either at the liquid-air interface or just below the surface of the wet oil film. The peroxy radical thus formed can, in turn, either abstract a hydrogen atom from the activated position of another molecule of unsaturated acid to form a *hydroperoxide*<sup>40</sup> or add to the

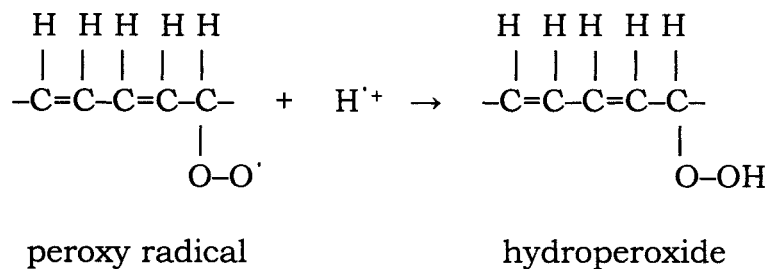
<sup>37</sup> All the unsaturated fatty acids containing two or more double bonds have the bonds separated by one or more methylene groups ( $-\text{CH}_2-$ ). These double bonds are called *unconjugated*. Accordingly, *conjugated* are the double bonds that have no methylene group between them [WINGROVE, A.S., CARET, R.L., *Organic Chemistry*, Harper & Row Publishers, New York (1981), p. 255].

<sup>38</sup> VAN DEN BERG, J.D.J., VAN DEN BERG, K.J., BOON, J.J., *Chemical Changes in Curing and Ageing Oil Paints*, in *ICOM Committee for Conservation, 12th Triennial Meeting, Lyon, 29 August - 3 September 1999: Preprints*, edited by J. Bridgland, Vol. I, James & James, London (1999), p. 248-249.

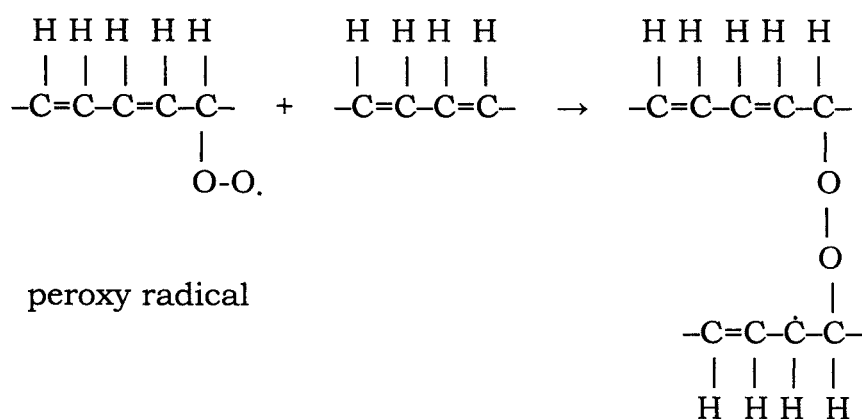
<sup>39</sup> The dot symbolises the single unpaired electron of the free radicals.

<sup>40</sup> See also PIRETTI, M., CAPELLA, P., PALLOTTA, U., *Contribution to the Study of Hydroperoxides Formation in the Course of Fats Autoxidation – Note 1*, *Rivista Italiana delle Sostanze Grasse*, 46 (1969), p. 652-658.

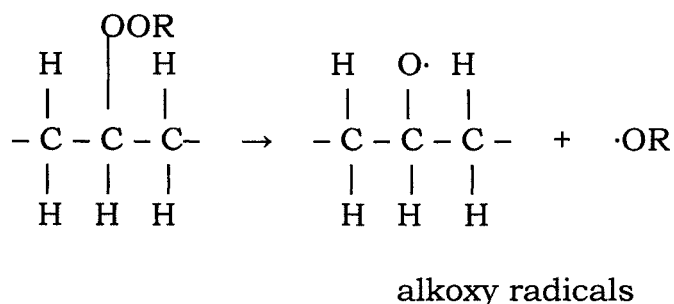
double bonds of another triglyceride molecule that contains conjugated diene groups:



or



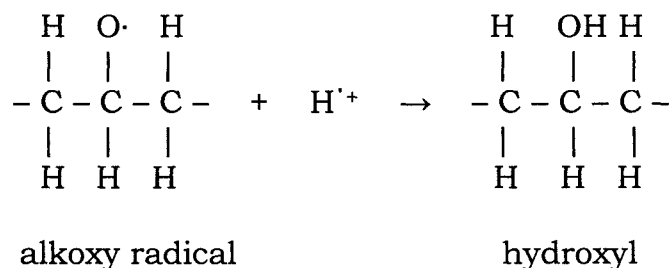
The above dimer linked by a peroxy group may react further in various ways until it reaches a non-radical product. Both hydroperoxy and peroxy groups are rather unstable and may decompose to give new radicals. Hence, they can split up and form *alkoxy* radicals <sup>41</sup>:



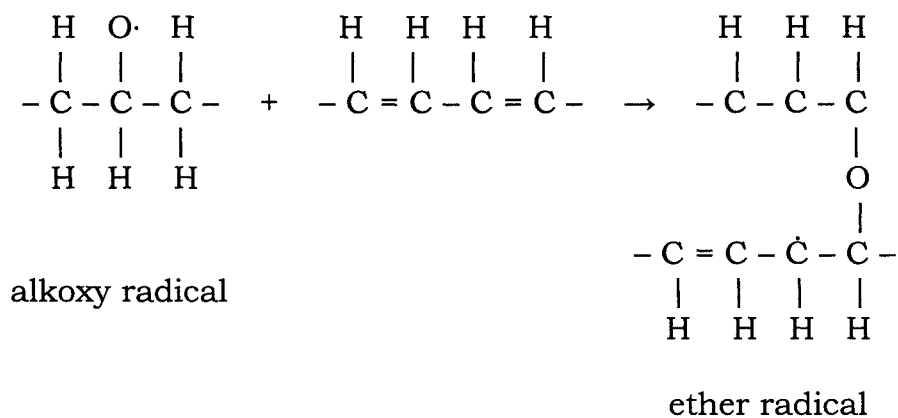
<sup>41</sup> This reaction is called *homolysis* [FRANKEL, E.N., *Lipid Oxidation*, The Oily Press, Dundee (1998), p. 7-8].



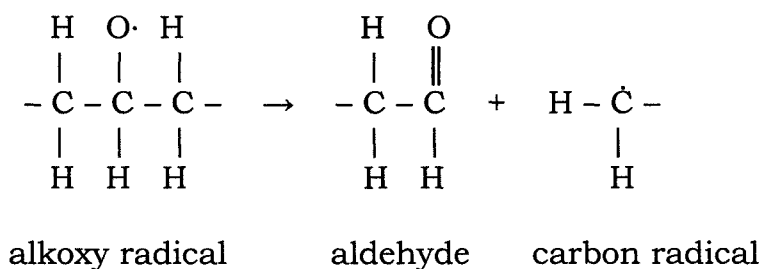
Alkoxy radicals can either react as the peroxy radicals in the ways described to yield stable *hydroxyl* groups or *ether* linkages, or can undergo decomposition that leads to the formation of *aldehydes*:



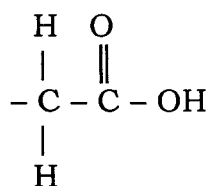
or



or

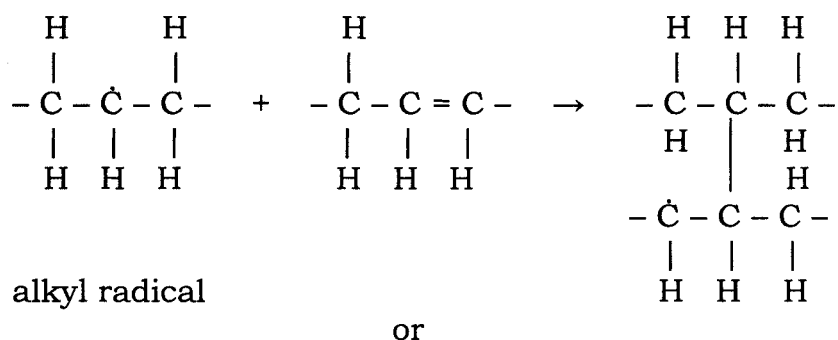


The last reaction leads to scission of carbon-carbon fatty acid chains and consequent breakage of the triglycerides into smaller fragments. The carbon radical may go on to react with oxygen or add to double bounds, while aldehydes can be further oxidised to carboxylic acids:

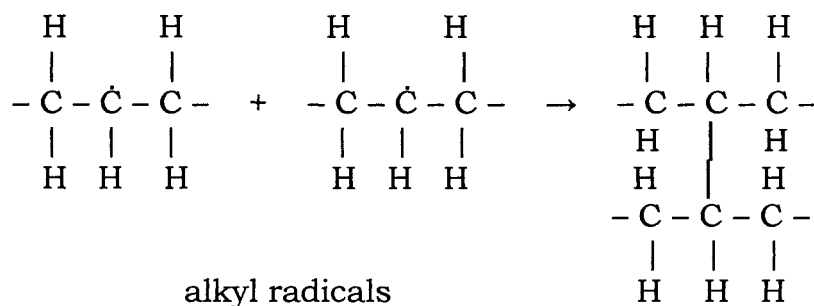


If the original alkoxy radical derives from the ester end of a fatty acid chain then the resulting acid is the half ester of a dicarboxylic acid. Accordingly, if the alkoxy radical derives from the hydrocarbon end of the fatty acid chain, the product is a mono-carboxylic acid. The length of these two potential products is dependant on the exact position of the hydroperoxy group on the eighteen-carbon fatty acid chain (linoleic and linolenic acids). Usually this results from oxidation of a double bond at C<sub>9</sub><sup>42</sup> and, therefore, the main products are the half esters of the nine-carbon dicarboxylic acid (i.e. azelaic acid). The eight- and ten-carbon dicarboxylic acids (i.e. suberic and sebacic acids), and the nine-carbon mono-carboxylic acid product can also be formed.

Apart from the above reactions that take place in the presence of oxygen and result in peroxy and oxy linkages between the fatty-acid molecules, Mills & White explain that some secondary reactions leading to the creation of carbon-carbon bonds may also occur, particularly in conditions of low oxygen concentration. Thus, an *alkyl* radical may either attack the double bond of another molecule to form a dimer that will continue to react in the same way or, less commonly, combine with another alkyl radical:



<sup>42</sup> That is the double bond closest to the carboxyl carbon in most unsaturated fatty acids of oils that derive from plants.



To summarise, during the drying process that constitutes the first stage of film formation of drying oils, the main reaction that occurs is formation of poly-peroxides.<sup>43</sup> These can undergo either scission to yield alkoxy radicals and to form ether linkages or degradation that results in breakdown of the cross-links and the fatty-acid chains. The short-chain alcohols, ketones, aldehydes and free fatty acids thus produced can evaporate if they are volatile enough. These compounds give the characteristic smell to a drying oil film.<sup>44</sup> In cases of low oxygen concentration, simultaneously with the above oxidation and degradation reactions, polymerisation may also occur resulting in the formation of carbon-carbon bonds.

The above free-radical chain-reaction mechanism has been discussed in terms of individual fatty acids. Yet drying oils are predominantly formed by triglycerides and each of them contains two or three unsaturated fatty acids. Hence, Mills & White note that after the formation of a dimer between two fatty acids from different triglycerides, these continue to react until the remaining unsaturated fatty acids create bonds with those present in other triglyceride molecules, a process that can potentially lead to development of a highly cross-linked network.<sup>45</sup>

<sup>43</sup> The oxidised product of linseed oil is known as *linoxyn* [See MAYER, R., *The Artist's Handbook of Materials and Techniques*, Faber and Faber, 5<sup>th</sup> Edition (1991), p. 465].

<sup>44</sup> See HANCOCK, R.A., LEEVES, N.J., *Studies in Autoxidation. Part I. The Volatile By-Products Resulting from the Autoxidation of Unsaturated Fatty Acid Methyl Esters*, *Progress in Organic Coatings*, 17 (1989), p. 321-336.

<sup>45</sup> MILLS, J.S., WHITE, R., *The Organic Chemistry of Museum Objects*, Butterworth-Heinemann, 2<sup>nd</sup> Edition, Oxford (1999), p. 38.

The dried-oil film thus formed has higher density and refractive index than the initial wet film. The increase in density indicates the high compactness and the presence in the system of bonds, whereas the increase in refractive index is indicative of the presence of polar groups or ring structures. In fact, the oil film contains large numbers of six-membered ring systems instead of the initial linear structure of the fatty acids.<sup>46, 47</sup> The original unsaturation and, consequently, the iodine number decreases considerably because of the reactions that involve the double bonds. At the same time there is a distinct increase in the oxygen content. To the above mentioned physical changes the increase in the ultra-violet and infrared absorption and the rapid decrease in specific refraction should also be added.<sup>48, 49, 50</sup>

After drying, the oil film undergoes further chemical changes that eventually lead to its degradation. Thus, the oxidation process of the already reacted double bonds proceeds and, at the same time, hydrolysis of the original ester linkages takes place. Both reactions result in the breakdown of the polymer matrix, an increase in the number of functional groups and the formation of low molecular-weight products. This phase is called the *mature stage* of the dried-oil film.<sup>51, 52</sup>

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<sup>46</sup> ERHARDT, D., *Paints Based on Drying-Oil Media*, in *Painted Wood: History and Conservation, Proceedings of a Symposium Organised by the Wooden Artifacts Group of the AIC, Williamsburg, Virginia 11-14 November 1994*, edited by V. Dorge and F.C. Howlett, The Getty Conservation Institute, Los Angeles (1998), p. 24-25.

<sup>47</sup> POTNIS, S.P., VENKATARAMAN, R., *Studies in Driers - I. Importance of Drier*, Paintindia, 14 (1964), p. 19.

<sup>48</sup> POWERS, P.O., OVERHOLT, J. L., ELM, A.C., *Formation and Deterioration of Paint Films: Polymerization of the Vinyl Type in the Drying of Oils*, Industrial and Engineering Chemistry, 33 (1941), p. 1259-1263.

<sup>49</sup> VAN DEN BERG, J.D.J., *Analytical Chemical Studies on Traditional Linseed Oil Paints*, PhD Thesis, FOM-Institute AMOLF, University of Amsterdam (2002), p. 42-45.

<sup>50</sup> VAN DER WEERD, J., *Microscopic Analysis of Traditional Oil Paint*, PhD Thesis, FOM-Institute AMOLF, University of Amsterdam (2002), p. 79-84.

<sup>51</sup> ELM, A.C., *Deterioration of Dried Oil Films*, Industrial and Engineering Chemistry, 41 (1949), p. 319-324.

<sup>52</sup> VAN DEN BERG, J.D.J., VAN DEN BERG, K.J., BOON, J.J., *Chemical Changes in Curing and Ageing Oil Paints*, in *ICOM Committee for Conservation, 12th Triennial Meeting, Lyon, 29 August - 3 September 1999: Preprints*, edited by J. Bridgland, Vol. I, James & James, London (1999), p. 248-249.

According to Van den Berg *et al.*, the products of the oxidative polymerisation formed during drying are subject to continued oxidation, especially at the sites of carbon-oxygen bonds. This involves oxidative cleavage of the fatty acid hydrocarbon chains and an increase in the number of oxygen-containing functional groups, such as hydroxyl and carboxyl groups. Continued oxidation may also produce the same small mobile molecules that are formed during the drying process by the breakage of cross-links and fatty-acid chains. Thus, the amount of azelaic acid found immediately after drying increases during ageing. These molecules may migrate to the film surface and ultimately evaporate causing a loss of weight.<sup>53</sup>

As Van den Berg *et al.* also explain, the hydrolysis of ester linkages of triglycerides results in their cleavage to yield alcohols and carboxylic acids. The alcohols are likely to be attached to the polymeric lattice through other ester linkages with fatty acid groups. The carboxylic acids may join the dried-oil matrix by forming bonds with other triglycerides, unless they are saturated and therefore have not reacted or were unsaturated and have undergone scission. In those cases hydrolysis can yield the original saturated acids, short-chain fatty acids or scission products such as hydroxy acids and diacids. The transition from the initial polyester to a form of polyanionic polymer system in ageing of dried-oil films, however, is still not fully understood.

The above chemical changes also affect the appearance of the dried-oil film by rendering it harder and darker. Extremely degraded films, however, can soften as low molecular-weight components present in increasing amounts due to ageing function as plasticisers, an effect known as *syneresis*. Loss of those components through evaporation causes shrinkage of the film, which becomes stiffer and acquires a

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<sup>53</sup> See also SLANSKY, P., *The Drying and Ageing of Linseed Oil Films: Some Aspects of the Formation of Volatile Compounds*, Paint Manufacture, 19 (1949), p. 113-114 & 117.

lighter and dull colour. This is the final phase of ageing of the dried-oil film and is called the *degradation stage*.<sup>54</sup>

Yellowing, especially when oil films are kept in the dark, is another important phenomenon of deterioration that occurs in drying oils: Elm studied the drying of trilinolenic glyceride in relation to yellowing;<sup>55</sup> Laurie made some notes on the yellowing of linseed oil;<sup>56</sup> Rakoff *et al.* examined the influence of linolenate content on the yellowing of linseed-oil paints;<sup>57</sup> Kumarathasan *et al.* investigated the autoxidation and yellowing of methyl linolenate.<sup>58</sup> In the latest study, however, Mallégol *et al.* have examined the cause of yellowing of oil-based paints and have found that this can be attributed to co-oxidation reactions of contaminants. Moreover, they concluded that the yellowing level is closely related to the extent of drying and appears to be unaffected by the linolenate content.<sup>59</sup>

The various aspects of the drying and ageing mechanisms of drying oils have been the subject of many studies in the past. A few authors whose published work can be stated in this context, starting from the first decades of the 20<sup>th</sup> century, are Bradley,<sup>60</sup> Wexler,<sup>61</sup> Ingold,<sup>62</sup>

<sup>54</sup> ERHARDT, D., *Paints Based on Drying-Oil Media*, in *Painted Wood: History and Conservation, Proceedings of a Symposium Organised by the Wooden Artifacts Group of the AIC, Williamsburg, Virginia 11-14 November 1994*, edited by V. Dorge and F.C. Howlett, The Getty Conservation Institute, Los Angeles (1998), p. 23-24.

<sup>55</sup> ELM, A.C., *The Drying and Yellowing of Trilinolenic Glyceride*, *Industrial and Engineering Chemistry*, 23 (1931), p. 881-886.

<sup>56</sup> LAURIE, A.P., *Notes - The Yellowing of Linseed Oil*, *Technical Studies in the Field of the Fine Arts*, 4 (1936), p. 145.

<sup>57</sup> RAKOFF, H., THOMAS, F.L., GAST, L.E., *Yellowing and Other Film Properties of Linseed-Derived Paints Influenced by Linolenate Content*, *Journal of Coatings Technology*, 48 (1976), p. 55-57.

<sup>58</sup> KUMARATHASAN, R., RAJKUMAR, A.B., HUNTER, N.R., GESSER, H.D., *Autoxidation and Yellowing of Methyl Linolenate*, *Progress in Lipid Research*, 31 (1992), p. 109-126.

<sup>59</sup> MALLÉGOL, J., LEMAIRE, J., GARDETTE, J.L., *Yellowing of Oil-Based Paints*, *Studies in Conservation*, 46 (2001), p. 121-131.

<sup>60</sup> BRADLEY, T.F., *Drying Oils and Resins: Mechanism of the 'Drying' Phenomenon*, *Industrial and Engineering Chemistry*, 29 (1937), p. 440-445.

<sup>61</sup> WEXLER, H., *The Polymerisation of Drying Oils*, *Chemical Reviews*, 64 (1964), p. 591-611.

<sup>62</sup> INGOLD, K.U., *Peroxy Radicals*, *Accounts of Chemical Research*, 2 (1969), p. 1-9.

Hutchinson <sup>63</sup>, Formo <sup>64</sup>, Chan <sup>65</sup> and Schaich <sup>66</sup>; Namar *et al.* <sup>67</sup>, Grosch <sup>68</sup> and Frenkel <sup>69</sup> have given an extensive review on the oxidation products of lipid material. The largest amount of experimental data exists for linseed oil; among others, Poisson <sup>70</sup> investigated its oxidation and Toussaint *et al.* <sup>71</sup> examined its drying and thermal polymerisation as evident in infrared spectra. Finally, Boon *et al.* <sup>72</sup> and van den Berg *et al.* <sup>73</sup> have recently studied some aspects of the ageing of oil-paint films, using GC/MS (Gas Chromatography/Mass Spectrometry) and DTMS (Direct Temperature Resolved Mass Spectrometry).

During drying and ageing the absorption of oxygen is initially slow, <sup>74</sup> then becomes more rapid for some time and gradually the rate diminishes until completion of the process. The total increase of weight due to oxidation can be calculated from the absorption of oxygen less

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<sup>63</sup> HUTCHINSON, G.H., *Some Aspects of Drying Oils Technology*, Journal of the Oil and Colour Chemists' Association, 56 (1973), p. 44-53.

<sup>64</sup> FORMO, M.W., *Paints, Varnishes and Related Products*, in *Bailey's Industrial Oil and Fat Products*, edited by D. Swern, Vol. 1, John Wiley & Sons, 4<sup>th</sup> Edition, N. York (1979), p. 687-816.

<sup>65</sup> CHAN, H.W.S., *The Mechanism of Autoxidation*, in *Autoxidation of Unsaturated Lipids*, edited by H.W.S. Chan, Food Science and Technology, Academic Press, London (1987), p. 1-16.

<sup>66</sup> SCHAICH, K.M., *Metal and Lipid Oxidation - Contemporary Issues*, Lipids, 27 (1992), p. 209-218.

<sup>67</sup> NAMAR, W.W., WITCHWOOT, A., *Autoxidation of Oil and Fats at Elevated Temperatures*, in *Autoxidation in Food and Biological Systems*, edited by M. G. Simic and M. Karel, Plenum Press, New York (1980), p. 207-221.

<sup>68</sup> FRANKEL, E.N., *Lipid Oxidation*, The Oily Press, Dundee (1998), p. 55-77.

<sup>69</sup> GROSCH, W., *Reactions of Hydroperoxides - Products of Low Molecular Weight*, in *Autoxidation of Unsaturated Lipids*, edited by H.W.S. Chan, Academic Press, London (1987), p. 95-140.

<sup>70</sup> POISSON, R., *Contribution à l' Étude du Phénomène de Siccativité de l' Huile de Lin*, Peintures, Pigments, Vernis, 42 (1966), p. 588-602.

<sup>71</sup> TOUSSAINT, A., APRIL, A., *Mise au Point du Phénomène de Séchage des Huiles et de Leur Polymérisation Thermique en Vue de l' Étude du Jaunissement*, FATIPEC Congress, 7 (1964), p. 19-32.

<sup>72</sup> BOON, J. J., PEULVÉ, S. L., VAN DEN BRINK, O. F., DUURSMA, M. C., RAINFORD, D., *Molecular Aspects of Mobile and Stationary Phases in Ageing Tempera and Oil Paint Films in Early Italian Paintings: Techniques and Analysis, Symposium, Maastricht, 9-10 October 1996*, Limburg Conservation Institute, Maastricht (1997), p. 35-56

<sup>73</sup> VAN DEN BERG, J.D.J., VAN DEN BERG, K.J., BOON, J.J., *Chemical Changes in Curing and Ageing Oil Paints in ICOM Committee for Conservation, 12th Triennial Meeting, Lyon, 29 August - 3 September 1999: Preprints*, edited by J. Bridgland, Vol. I, James & James, London (1999), p. 248-253.

<sup>74</sup> This initial phase is called *induction period*.

the diminution resulting from the escape of the volatile decomposition products.<sup>75, 76, 77, 78</sup>

The mechanisms of drying and ageing may be influenced by several factors.<sup>79</sup> Weather conditions and, in particular, humidity affect the rate of drying of oil films. Experiments run on samples of linseed oil have demonstrated that high humidity inhibits the rate of oxygen absorption and therefore the drying of the oil.<sup>80</sup> Furthermore, the rate of drying depends on the temperature, the thickness of the oil film, the presence of light<sup>81</sup> and on the substrate on which the oil is painted.<sup>82</sup> Formation of a dried-oil film may also occur in the absence of oxygen or even when the environment is not exposed to light provided there is sufficient gas pressure. This means that atmospheric pressure plays an important part in the formation of dried-oil films.<sup>83</sup>

<sup>75</sup> EIBNER, A., *Über Fette Öle*, B. Heller, Munich (1922), p. 30.

<sup>76</sup> GETTENS, R.J., STOUT, G.L., *Paintings Material: A Short Encyclopaedia*, Dover Publications, Inc., New York (1966), p. 39.

<sup>77</sup> MARLING, P.E., *Effect of Various Driers on Linseed Oil Films During Aging*, Industrial and Engineering Chemistry, 21 (1929), p. 346-347.

<sup>78</sup> LAZZARI, M., CHIANTORE, O., *Drying and Oxidative Degradation of Linseed Oil*, Polymer Degradation and Stability, 65 (1999), p. 303-313.

<sup>79</sup> LONG, J.S., RHEINECK, A.E., BALL, G.L., *Studies in the Drying Oils. XVII. Influence of Several Factors on the Mechanism of Drying of Oil Films*, Industrial and Engineering Chemistry, 25 (1933), p. 1086-1091.

<sup>80</sup> MUKHERJEA, R.N., GUPTA, K. S., *Effect of Driers on Autoxidation and Film Formation of Drying oils – 2. Influence of Humidity*, Paintindia, 13 (1963), p. 19-21.

<sup>81</sup> GARDNER, H.A., PARKS, H.C., *Notes on the Influence of Coloured and Ultra-Violet Light on the Drying Time of Linseed Oil and Varnish*, Paint Manufacturers' Association of the U.S. – Circular, 172 (1923), p. 148-151.

<sup>82</sup> MILLER, C.D., *Studies of the Oxidation of Absorbed Polymer*, American Chemical Society, Division of Polymer Chemistry, Preprints, 8 (1967), p. 1203-1210.

<sup>83</sup> POTNIS, S.P., VENKATARAMAN, R., *Studies in Driers - I. Importance of Drier*, Paintindia, 14 (1964), p. 19-23.



### C. Effects of Heat Bodying and Driers

In order to produce a more viscous, occasionally faster drying oil that possesses a higher degree of tackiness <sup>84</sup> it can be subjected to heat treatment or so-called *heat bodying* in the presence or absence of oxygen. The product is a drying oil in which the linking of its triglycerides is already partially effected before it is put into use, hence the general term *pre-polymerised oil*. In the absence of oxygen thermal polymerisation is the main reaction that takes place generating a thickened, known today (since the 19<sup>th</sup> century) as *stand oil*. <sup>85, 86</sup> The viscosity of a raw oil can be enhanced and the drying time significantly reduced by blowing oxygen through it during heating, in which case the reactions that take place are thought to be much the same as during air-drying of unheated oils. These reactions depend on the airflow, turbulence (degree and type of agitation) and the temperature of the process, and yield the so-called *blown oil*. <sup>87, 88</sup> Heating at high temperatures, however, leads to darkening and decomposition of the oil, also called *boiled oil*. <sup>89</sup> Drying oils for use in painting were often subjected to photochemical reactions by exposure to the sun, hence the term *sun-thickened oil*. <sup>90</sup>

When heated at moderate temperatures and in the absence of oxygen, the drying oil undergoes thermal excitation of its polyene system. Isomerisation of the positions of the double bonds to more reactive configurations, namely conjugated double bonds, takes place. When conjugated dienes are involved in the reactions the rate of the

<sup>84</sup> VOET, A., *Dynamics of Tackiness in Higher Molecular Materials*, Bulletin de la Société Chimique de France (1970), p. 3255-3258.

<sup>85</sup> BALBI, G., *Gli Oli Cotti*, Olearia, 6 (1952), p. 144-153.

<sup>86</sup> MAYER, R., *The Artist's Handbook of Materials and Techniques*, Faber and Faber, 5<sup>th</sup> Edition (1991), p. 172-173.

<sup>87</sup> BALBI, G., *Gli Oli Soffiati*, Olearia, 6 (1952), p. 335-345.

<sup>88</sup> MAYER, R., *The Artist's Handbook of Materials and Techniques*, Faber and Faber, 5<sup>th</sup> Edition (1991), p. 173.

<sup>89</sup> The term is now generally used to characterise a drying oil that has been heated with added chemical driers. See Ibidem, p. 173.

<sup>90</sup> Ibidem, p. 173-174.

polymerisation under thermal activation is even faster. In these systems inter-molecular as well as intra-molecular reactions occur, known as *Diels-Alder* additions, which result in the creation of new carbon-carbon linkages and to cyclisation. The inter-molecular reaction takes place between two fatty acid groups that belong to two separate triglycerides and causes dimerisation. On the other hand, the intra-molecular reaction occurs between two fatty acid groups that are part of the same triglyceride molecule and does not increase the molecular weight of the drying oil. In addition to dimer formation, cyclic monomeric acids are also formed, which almost certainly go on to be incorporated into the polymer network. Depending on the unsaturation and the relative positions of the double bonds, cyclic C<sub>18</sub> fatty acids containing saturated or unsaturated cyclic rings of five or six atoms will be formed. In the case of un-conjugated polyenes present in the system, an induction period is required before the formation of ring systems can occur. During this period, isomerisation of the un-conjugated polyenes to the conjugated system takes place.<sup>91, 92, 93, 94, 95, 96</sup>

When stand oils are laid out in a thin film, they dry more slowly than raw oils and the amount of oxygen that they take up is much less than for oxidatively dried-oil films (about 3% by weight). Accordingly, less oxygen in the system means less inclination to further oxidation and,

<sup>91</sup> McINNES, A.G., COOPER, F.P., MacDONALD, J.A., *Further Evidence for Cyclic Monomers in Heated Linseed Oil*, Canadian Journal of Chemistry, 39 (1961), p. 1906-1914.

<sup>92</sup> GAST, L.E., SCHNEIDER, W.J., FOREST, C.A., COWAN, J.C., *Composition of Methyl Esters from Heat-Bodied Linseed Oils*, Journal of the American Oil Chemists' Society, 40 (1963), p. 287-289.

<sup>93</sup> BOELHOUWER, C., KNEGTEL, J. T., TELS, M., *On the Mechanism of the Thermal Polymerisation of Linseed Oil*, Fette, Seifen, Anstrichmittel, 69 (1967), p. 432-436.

<sup>94</sup> FRIEDERICH, J.P., *C<sub>18</sub>-Saturated Cyclic Acids from Linseed Oil. A Structural Study*, Journal of the American Oil Chemists' Society, 44 (1967), p. 244-248.

<sup>95</sup> SÉBÉDIO, J.L., GRANDGIRARD, A., *Cyclic Fatty Acids: Natural Sources, Formation During Heat Treatment, Synthesis and Biological Properties*, Progress in Lipid Research, 28 (1989), p. 303-336.

<sup>96</sup> MARTIN, J.C., NOUR, M., LAVILLONNIÈRE, F., SÉBÉDIO, J.L., *Effect of Fatty Acid Positional Distribution and Triacylglycerol Composition on Lipid By-Products Formation During Heat Treatment: I. Polymer Fraction, II. Trans Isomers III. Cyclic Fatty Acid Monomers Study*, Journal of the American Oil Chemists' Society, 75 (1998), p. 1065-1071, 1073-1078 & 1691-1697.

therefore, enhanced durability of the dried-oil film. Furthermore, stand oils are less prone to yellowing due to the reduction of the linolenic acid content and undergo smaller volume changes on drying, resulting in less wrinkling.<sup>97</sup>

The physical and chemical changes of heat-bodied drying oils have been investigated by a number of researchers in the past decades. Seavell *et al.* examined the effects of various factors on the heat bodying of linseed oil;<sup>98</sup> Hess *et al.*<sup>99</sup> and Pokorný<sup>100</sup> investigated the oxidation of blown linseed oil at various temperatures, and Gillam subdivided the oxidation reactions with temperature into four types<sup>101</sup>; Fedeli *et al.* studied the thermal polymerisation of heat-bodied linseed oil.<sup>102, 103</sup> Finally, Figge has given a literature review on the mechanisms and products of the thermal reactions of unsaturated fatty acid esters.<sup>104</sup>

The physical changes that occur during the heat-bodying process mainly regard certain values such as viscosity, density, acid value, refraction index and iodine number. When heating takes place the viscosity is increased due to changes in the molecular weight of the

<sup>97</sup> MILLS, J.S., WHITE, R., *The Organic Chemistry of Museum Objects*, Butterworth-Heinemann, 2<sup>nd</sup> Edition, Oxford (1999), p. 41.

<sup>98</sup> SEAVELL, A.J., SLEIGHTHOLME, J.J., *Factors Affecting the Heat Thickening of Linseed Oil*, Journal of the Oil and Colour Chemists' Association, 36 (1953), p. 119-126.

<sup>99</sup> HESS, P.S., O'HARE, G.A., *Oxidation of Linseed Oil: Temperature Effects*, Industrial and Engineering Chemistry, 42 (1950), p. 1424-1431.

<sup>100</sup> POKORNÝ, J., *A Study of Autoxidation of Some Vegetable Oils at Elevated Temperatures: XII. The Effect of Reactive and Unreactive Peroxides on the Velocity of Autoxidation of Blown Linseed Oil Films*, Scientific Papers from Institute of Chemical Technology, Prague Food Technology, 6 (1962), p. 267-273.

<sup>101</sup> GILLAM, N.W., *Variation of Chemical Reactions with Temperature During the Oxidation and Polymerization of Fatty Oils*, Australian Chemical Institute Journal and Proceedings, 16 (1949), p. 22-36.

<sup>102</sup> FEDELI, E., CAPELLA, P., VALENTINI, A.F., *Accrescimento Molecolare dei Termopolimeri dell'Olio di Lino - Nota III*, Rivista Italiana delle Sostanze Grasse, 40 (1963), p. 321-329.

<sup>103</sup> FEDELI, E., CAPELLA, P., VALENTINI, A.F., JACINI, G., *Ricerche sulla Termopolimerizzazione degli Oli Vegetali - Nota IV: Formazione di Acidi Trimeri nella Termopolimerizzazione dell'Olio di Lino*, Rivista Italiana delle Sostanze Grasse, 41 (1964), p. 647-651.

<sup>104</sup> FIGGE, K., *Dimeric Fatty Acid [1-<sup>14</sup>C] Methyl Esters. I. Mechanisms and Products of Thermal and Oxidative-Thermal Reactions of Unsaturated Fatty Acid Esters - Literature Review*, Chemistry and Physics of Lipids, 6 (1971), p. 164-182.

drying-oil components. The density is also increased. The acid values, indicating the presence of residues of free fatty acids and the refractive indices, indicative of the formation of new compounds in the oil, are both increased. Reduction of the number of unsaturated bonds leads to a continuous decrease of the iodine number. The changes of all the above values during the heat-bodding process are not uniform.<sup>105, 106</sup>

Some of the chemical changes that occur during heat bodding have been detected by infrared spectroscopy. Infrared spectra taken in different phases of the heating process have shown disappearance of the multiple double bonds accompanied by simultaneous appearance of the isolated *trans* double bond and a decrease in the number of carbon-carbon bonds. These chemical changes are due to the polymerisation of polyunsaturated groups that sets in after an induction period, along with the release of free fatty acids. Moreover, gas chromatographic analysis of the unpolymerised part of heat-bodied linseed oil has proved that there is a significant decrease of the linolic and linolenic acids (44% and 80% respectively), while only a small decrease is noted in the oleic acid.<sup>107</sup> Further analyses of bodied oils by gas chromatography have shown that various components of differing chain lengths have also been formed, consisting of oxygenated and dimer fatty acids. Analysis by both nuclear magnetic resonance and infrared spectroscopy has also shown the presence of a cyclohexene ring together with an ether linkage in which the latter one predominates.<sup>108</sup> Furthermore, a chromatic reaction method based on the research of aldehydes has revealed the oxidation products created during heat bodding.<sup>109</sup>

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<sup>105</sup> CARRICK, L.L., BOULGER, E.W., THOMPSON, L.J., *Drying of Air Blown, Heat-Treated Linseed Oil Films*, American Paint Journal, 25 (1941), p. 18-23 & 54-62.

<sup>106</sup> PASCUAL, O.S., DETERA, S.D., *A Study of the Heat Bodding Characteristics of a Drying Oil Mixture*, Philippines Nuclear Journal, 1 (1966), p. 29-31.

<sup>107</sup> Ibidem, p. 31-35.

<sup>108</sup> KOLEY, S.N., *Studies on a New Type of Bodied Oil II*, Fette, Seifen, Anstrichmittel, 73 (1971), p. 625-630.

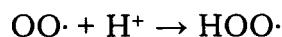
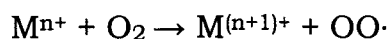
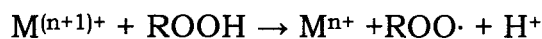
<sup>109</sup> PALUMBO, M., *Identificazione Degli Standoli, Vernici Litografiche, Olii Cotti ed Olii Soffiati Ottenuti dall' Olio di Lino*, Industria della Vernice, 6 (1952), p. 113-115.

Apart from heat bodying, the drying process of oils may also be affected by certain materials called *driers*, i.e. metal-containing compounds added to oils to accelerate their drying rate. In paintings these compounds are added to oils either specifically for their effect on the drying process or as artists' pigments. Metal-bearing compounds containing metals capable of existing in more than one valence state, such as copper, cobalt, lead, manganese and iron, can react in a catalytic cycle to promote the overall process of drying. The effects of driers on the intermediate steps of the drying process, however, are varied and complex. They catalyse the lipid oxidation by forming complexes with the carboxylic acid groups of the free fatty acids present. For example, metal-ion co-ordination of the fatty acid groups of the cross-linked material and non-cross-linked fractions occurs. These multivalent interactions lead to complex linkages between different parts of the polymer network.<sup>110</sup>

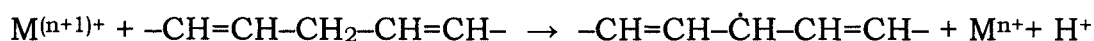
The major requirements in order for substances to act as driers are their solubility in drying oils and the availability of the metal for its "drier" action. A substance capable of acting as a drier must catalyse the oxidation process by increasing the solubility of oxygen into the film-forming materials, as well as by activating the oxygen, so that it can react with the double bonds of the system to form peroxides and hydroperoxides. The drier should also be able to decompose these peroxides and hydroperoxides to liberate free radicals, which are primarily responsible for the initiation of chain reactions leading to film formation. Shown below are the reactions that may occur in the presence of a drier, with M representing the metal that exists in two valences and acts as a *promoter*, and the hydroperoxide being the so-called *initiator*.

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<sup>110</sup> FRANKEL, E.N., *Lipid Oxidation*, The Oily Press, Dundee (1998), p. 20-21 & 172-174.



The first and the last reaction together provide a reduction-oxidation, or *redox* mechanism, which promotes polymerisation in closed systems without the intervention of oxygen. Direct oxidation of the methylene groups adjacent to or between double bonds is another possible reaction that requires a greater amount of energy.<sup>111, 112</sup>



There are a number of materials that meet the above requirements and can function in that dual capacity, however, occasionally it is necessary to use a combination of materials to achieve the desired rate of film formation. For instance, free radical donors and proton ( $H^+$ ) acceptors may be a good combination of substances to function as driers. Oil-soluble metal salts of organic compounds such as resinates, naphthenates and fatty acid soaps are often used as driers in commercial oil paints and varnishes. From all the above, it becomes clear that not all materials can be used effectively as driers for all the systems and under all conditions. Therefore, the choice of the right type of drier for a particular system under certain given conditions becomes an important issue. At elevated temperatures driers are also effective, provided that they can act as proton acceptors.<sup>113, 114, 115, 116</sup>

<sup>111</sup> Ibidem, p. 20.

<sup>112</sup> MILLS, J.S., WHITE, R., *The Organic Chemistry of Museum Objects*, Butterworth-Heinemann, 2<sup>nd</sup> Edition, Oxford (1999), p. 38-39.

<sup>113</sup> MARGIVAL, F., *Les Savons Métalliques et Leurs Applications en Peinture*, Peintures, Pigments, Vernis, 27 (1951), p. 352-355.

<sup>114</sup> MAYNE, J.E.O., RAMSHAW, E.H., *Autoxidation of the Lead Soaps of the Linseed Oil Fatty Acids*, Journal of Applied Chemistry, 13 (1963), p. 553-560.

<sup>115</sup> POTNIS, S.P., VENKATARAMAN, R., *Studies in Driers - I. Importance of Drier*, Paintindia, 14 (1964), p. 22-23.

<sup>116</sup> *Encyclopedia of Polymer Science and Engineering*, Vol. 5, John Wiley & Sons (1986), p. 207.

Certain traditional artists' pigments used in oil paints contain metal ions, such as lead and copper <sup>117, 118</sup> which have the required catalytic effect to act as driers. From experiments run on samples of clear linseed oil that were compared against samples of pigmented linseed oil where carbon black, Prussian blue and red lead have been used, it was found that the pigments significantly influence the oxygen absorption and the drying rate of linseed oil. After a storage period of four days the pigmented samples did not show any appreciable difference from the unpigmented ones. Yet, after storing the samples for four and eight months respectively, the results showed that all the pigments used for the preparation of the pigmented samples had a negative influence on oxygen absorption and on the drying time of linseed oil, apart from the sample containing red lead. The drying time of the red lead pigmented sample was shorter than that of the clear linseed oil film. <sup>119</sup>

Driers can affect the degradation process of a dried-oil film in the same way as they influence the drying, namely by catalysing the processes of oxidation and polymerisation. Nachtigal *et al.* have investigated the influence of pigments on the polymerisation of drying oils. <sup>120</sup> Rasti *et al.* have studied the effects of some pigments on the photo-oxidation of linseed oil films. They have shown that pigments cause remarkable differences in the rate of photo-oxidation of the same medium and under the same conditions. Furthermore, verdigris was proven to be an effective photo-stabiliser in the early stages and to have

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<sup>117</sup> IOAKIMOGLU, E. BOYATZIS, S., ARGITIS, P., FOSTIRIDOU, A., PAPAPANAGIOTOU, K., YANNOVITS, N., *Thin-Film Study on the Oxidation of Linseed Oil in the Presence of Selected Copper Pigments*, Chemistry of Materials, 11 (1999), p. 2013-2022.

<sup>118</sup> GUNN, M., CHOTTARD, G., RIVIÈRE, E., GIRERD, J.J., CHOTTARD, J.C., *Chemical Reactions Between Copper Pigments and Oleoresinous Media*, Studies in Conservation, 47 (2002), p. 12-23.

<sup>119</sup> MUKHERJEA, R.N., *Effect of Driers on Autoxidation and Film Formation of Drying Oils – III. Influence of Pigments*, Paintindia, 19 (1969), p. 32-34 & 40.

<sup>120</sup> NACHTIGAL, M., ZELINGER, J., *Effects of Various Factors in the Polymerisation and Degradation Process of Vegetable Oils Used in Art*, Chemicke Listy, 74 (1980), p. 1159-1184 and *The Influence of Pigments on the Polymerisation of Linseed Oil*, PICT Scientific Papers, S6 (1981), p. 119-156.

relatively little effect in the later stages.<sup>121</sup> Finally Mallégol *et. al.* have examined the effect of driers on the curing of linseed oil.<sup>122</sup>

A number of natural organic compounds may function as antioxidants, i.e. inhibitors of oxidation reactions. Pigments such as carbon black and bituminous earths contain phenols and, therefore, oils containing those pigments may either dry very slowly or not dry at all. Drying oils themselves contain a small amount of phenolic compounds, as well as tocopherols (vitamin E), which may both contribute to the induction period in the drying process.<sup>123</sup>

The detection and identification of drying oils can be achieved by qualitative and quantitative analysis of the component fatty acids. The best way of doing this is by means of gas chromatography in conjunction with mass spectrometry. In order to render fatty acids suitable for this method of analysis, these must be first converted to their more volatile methyl esters. The techniques of gas chromatography and mass spectrometry for the study of drying oils has been developed, amongst others, by Orr *et al.*,<sup>124</sup> O'Neill *et al.*,<sup>125</sup> Zaitoun,<sup>126</sup> Jamieson *et al.*,<sup>127</sup>

<sup>121</sup> RASTI, F., SCOTT, G., *The Effects of Some Common Pigments on the Photo-Oxidation of Linseed Oil-Based Paint Media*, Studies in Conservation, 25 (1980), p. 145-156 and *Mechanisms of Antioxidant Action: The Role of Copper Salts in the Photostabilisation of Paint Media*, European Polymer Journal, 16 (1980), p. 1153-1158.

<sup>122</sup> MALLÉGOL, J., LEMAIRE, J., GARDETTE, J.L., *Drier Influence on the Curing of Linseed Oil*, Progress in Organic Coatings, 39 (2000), p. 107-113.

<sup>123</sup> ERHARDT, D., *Paints Based on Drying-Oil Media*, in *Painted Wood: History and Conservation, Proceedings of a Symposium Organised by the Wooden Artifacts Group of the AIC, Williamsburg, Virginia 11-14 November 1994*, edited by V. Dorge and F.C. Howlett, The Getty Conservation Institute, Los Angeles (1998), p. 23.

<sup>124</sup> ORR, C.H., CALLEN, J.E., *Separation of Polyunsaturated Fatty Acid Methyl Esters by Gas Chromatography*, Journal of the American Chemical Society, 80 (1958), p. 249.

<sup>125</sup> O'NEIL, L.A., RYBICKA, S.M., *Examination of Unsaturated Glyceride Oils by Gas Chromatography*, Chemistry and Industry, March 9 (1963), p. 390-392.

<sup>126</sup> ZAITOUN, G., *Analyse Qualitative des Ester Méthyliques ou Éthyliques d'Acides Gras par Chromatographie en Phase Gazeuse*, Peintures, Pigments, Vernis, 42 (1966), p. 224-226.

<sup>127</sup> JAMIESON, G.R., REID, E.H., *The Analysis of Oils and Fats by Gas Chromatography III. Separation Factors of Acetates, Alcohols and Hydrocarbons*, Journal of Chromatography, 26 (1967), p. 8-16.



Novitskaya *et al.*,<sup>128</sup> Jernejčič *et al.*,<sup>129</sup> Capella *et al.*,<sup>130</sup> Christie,<sup>131</sup> Chaurasia *et al.*,<sup>132</sup> and Muizebelt *et al.*<sup>133</sup>.

The combination of the two techniques have lead to the solution of many problems concerning the identification of drying oils in the media of works of art and the properties of these films as they age. The application of the techniques of gas chromatography and mass spectrometry to such studies has been presented by Stolow *et al.*,<sup>134</sup> Mills & White,<sup>135</sup> Simon & Vigliano,<sup>136</sup> Kopecká,<sup>137</sup> Bucifalová,<sup>138</sup>

<sup>128</sup> NOVITSKAYA, G.V., VERESHCHAGIN, A.G., *The Chromatographic Separation of Higher Fatty Acid Monoglycerides According to Chain Length and Unsaturation*, Journal of Chromatography, 40 (1969), p. 422-430.

<sup>129</sup> JERNEJČIČ, M., PREMUR, L., *Analysis of Vegetable Oil Mixtures by Gas Chromatography*, Journal of the Oil and Colour Chemists' Association, 52 (1969), p. 623-627.

<sup>130</sup> CAPELLA, P., PIRETTI, M., STROCCHI, A., *Contribution to the Study of Hydroperoxide Formation in the Course of Fats Autoxidation. Note II. GC-MS of the Reaction Products*, Rivista Italiana delle Sostanze Grasse, 46 (1969), p. 659-667.

<sup>131</sup> CHRISTIE, W.W., *Gas Chromatography and Lipids - A Practical Guide*, The Oily Press, Ayr (1992).

<sup>132</sup> CHAURASIA, C.S., WILLIAMS, T.D., JUDSON, C.M., HANZLIK, R.P., *Quantitation of Fatty Acids and Hydroxy Fatty Acids by Gas Chromatography/Mass Spectrometry. Predictively Useful Correlations of Relative Response Factors with Empirical Formula*, Journal of Mass Spectrometry, 30 (1995), p. 1018-1022.

<sup>133</sup> MUIZEBELT, W.J., NIELEN, M.W.F., *Oxidative Crosslinking of Unsaturated Fatty Acids Studied with Mass Spectrometry*, Journal of Mass Spectrometry, 31 (1996), p. 545-554.

<sup>134</sup> STOLOW, N., *The Application of Gas Chromatography in the Investigation of Works of Art in Seminar on Application of Science in Examination of Works of Art*, Boston, September 7-16, 1965, Museum of Fine Arts, Boston, p. 172-183 and STOLOW, N., ROGERS, G.deW., *Gas Chromatography and Pyrolysis Techniques to Establish Ageing Characteristics of Works of Art in Seminar on Application of Science in Examination of Works of Art*, Boston, June 15-19, 1970, Museum of Fine Arts, Boston, p. 213-228.

<sup>135</sup> MILLS, J.S., *The Gas Chromatographic Examination of Paint Media: Part I. Fatty Acid Composition and Identification of Dried Oil Films*, Studies in Conservation, 11 (1966), p. 92-108 and MILLS, J.S., WHITE, R., *The Gas Chromatographic Examination of Paint Media. Some Examples of Medium Identification in Paintings by Fatty Acid Analysis in Conservation and Restoration of Pictorial Art*, edited by N.S. Brommelle and P. Smith, International Institute for Conservation of Historic and Artistic Works, Butterworths, London (1976) and *Organic Mass-Spectrometry of Art Materials: Work in Progress*, National Gallery Technical Bulletin, 6 (1982), p. 3-18.

<sup>136</sup> SIMON, J., VIGLIANO, M.G., *Applicazione della Gas-Cromatografia allo Studio della Composizione degli Oli Essicanti in Problemi di Conservazione*, a cura di G. Urbani, Editrice Compositori, Bologna (1973), p. 259-267.

<sup>137</sup> KOPECKÁ, I., *Determination of Drying Oils by Means of Gas Chromatography*, Sborník Restaurátorských Prací, 1 (1983), p. 91-98.

<sup>138</sup> BUCIFALOVÁ, J., *Chromatographic Methods to Determine Oils Used in Painting Techniques*, Sborník Restaurátorských Prací, 2-3 (1988), p. 64-77.

Nowik,<sup>139</sup> Casoli *et al.*,<sup>140</sup> Schilling *et al.*,<sup>141</sup> Colombini *et al.*<sup>142</sup> and van den Berg *et al.*<sup>143</sup>. Matteini *et al.* have examined the binders used in paintings by pyrolysis gas chromatography;<sup>144</sup> Carbinì *et al.* have applied Curie-point pyrolysis gas chromatography/mass spectrometry to different model paint samples containing linseed oil media<sup>145</sup> and Johnson *et al.* have reported that dried oils in paint films can be detected by thin-layer chromatography (TLC) of their non-saponifiable fraction<sup>146</sup>. Panek *et al.* have investigated the autoxidation of fats and oils using high performance liquid chromatography (HPLC)<sup>147</sup>. Fatty

<sup>139</sup> NOWIK, W., *Acides Amines et Acides Gras sur un Mème Chromatogramme - Un Autre Regard sur l'Analyse des Liants en Peinture*, Studies in Conservation, 40 (1995), p. 120-126.

<sup>140</sup> CASOLI, A., MUSINI, P.C., PALLA, G., Gas Chromatographic-Mass Spectrometric Approach to the Problem of Characterizing Binding Media in Paintings, Journal of Chromatography A, 731 (1996), p. 237-246.

<sup>141</sup> SCHILLING, M.R., KHANJIAN, H.P., *Gas Chromatographic Determination of the Fatty Acid and Glycerol Content of Lipids: I. The Effects of Pigments and Aging on the Composition of Oil Paints in ICOM Committee for Conservation, 11th Triennial Meeting in Edinburgh, Scotland, 1-6 September 1996: Preprints*, edited by J. Bridgland, Vol. I, James & James, London (1996), p. 220-227 and SCHILLING, M.R., KHANJIAN, CARSON, D.M., *Fatty Acid and Glycerol Content of Lipids; Effects of Ageing and Solvent Extraction on the Composition of Oil Paints*, *Techne*, 5 (1997), p. 71-78.

<sup>142</sup> COLOMBINI, M.P., MODUGNO, F., GIACOMELLI, M., FRANCESCONI, S., *Characterisation of Proteinaceous Binders and Drying Oils in Wall Painting Samples by Gas Chromatography-Mass Spectrometry*, Journal of Chromatography A, 846 (1999), p. 113-124.

<sup>143</sup> VAN DEN BERG, J.D.J. VAN DEN BERG, K.J., BOON, J.J., *Determination of the Degree of Hydrolysis of Oil Paint Samples Using a Two-Step Derivatisation Method and On-Column GC/MS*, Progress in Organic Coatings, 41 (2001), p. 143-155 and GC/MS Analysis of Fractions of Cured and Aged Drying Oil Paint, Advances in Mass Spectrometry 14: DO5 THPO121.

<sup>144</sup> MATTEINI, M., MOLES, A., MASALA, A., PARRINI, V., *Examination Through Pyrolysis Gas Chromatography of Binders Used in Painting*, in *Scientific Methodologies Applied to Works of Art, Symposium, Florence, Milan* (1986), p. 41-44.

<sup>145</sup> CARBINI, M., VOLPIN, S., TRALDI, P., *Curie-Point Pyrolysis Gas Chromatography/Mass Spectrometry in the Identification of Paint Media*, Organic Mass Spectrometry, 29 (1994), p. 561-565.

<sup>146</sup> JOHNSON, M., PACKARD, E., *Methods Used for the Identification of Binding Media in Italian Paintings of the Fifteenth and Sixteenth Centuries*, Studies in Conservation, 16 (1971), p. 145-164 and JOHNSON, M., ROSENBERG, H.E., SKOWRONSKI, R.P., *Thin-layer Chromatography of Sterols on Magnesium Trisilicate*, Studies in Conservation, 16 (1971), p. 165-167.

<sup>147</sup> PANEK, J., POKRONY, J., DAVIDEK, J., *Investigation of Changes of Fats and Oils During their Autoxidation*, New Approaches in Chromatography '91, Intercongress, Budapest, (1992), p. 145-158.

acids and their triglycerides have also been investigated using nuclear magnetic resonance (NMR) <sup>148</sup>.

Infrared spectrometry is another important tool for the study of drying oils and the changes that they undergo in the course of drying. In addition to its use in the characterisation and monitoring of the processes of oxidation and drying, infrared instrumentation has also been used in attempts to study the yellowing which occurs almost invariably in the process of ageing. It has also been applied to the identification of individual products after chromatographic separation, especially in conjunction with mass spectrometry, and to attempts to characterise the dried film. More recently, infrared Fourier transform (FT-IR) and Fourier transform Raman (FT-Raman) spectroscopies have improved the resolution of the instrumentation enabling the detection of small differences between commercial paint films as well as a reduction in the amount of sample needed for analysis. <sup>149</sup> Infrared microscopy has also been used on samples taken from the surfaces of paintings on canvas in efforts to identify paint media and pigments. Laser Raman spectroscopy shows a heightened sensitivity to carbon-carbon unsaturation and may prove a useful method in conjunction with infrared. The infrared absorption spectra of drying oils and paints have been examined by Gamble *et al.*, <sup>150</sup> Honn *et al.*, <sup>151</sup> Nicholls *et al.*, <sup>152</sup>

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<sup>148</sup> JOHNSON, L.F., SHOOLERY, J.N., *Determination of Unsaturation and Average Molecular Weight of Natural Fats by Nuclear Magnetic Resonance*, Analytical Chemistry, 34 (1962), p. 1136-1139 and HORVAT, R.J., McFADDEN, W.H., NG, H., LUNDIN, R.E., LANE, W.G., SHEPHERD, A.D., *Identification of Methyl Octanoate Derivatives from Autoxidised Methyl Linoleate by Mass Spectrometry*, Nuclear Magnetic Resonance and Infra-red Spectroscopy, Nature, 211 (1966), p. 298-299.

<sup>149</sup> MALLÉGOL, J., GARDETTE, J.L., LEMAIRE, J., *Long-Term Behavior of Oil-Based Varnishes and Paints I. Spectroscopic Analysis of Curing Drying Oils*, Journal of American Oil Chemists' Society, 76 (1999), p. 967-976.

<sup>150</sup> GAMBLE, D.L., BARNETT, C.E., *Infrared Absorption Spectra of Drying Oils*, Industrial and Engineering Chemistry, 32 (1940), p. 375-378.

<sup>151</sup> HONN, F.J., BEZMAN, I.I., DAUBERT, B.F., *Infrared Absorption of Hydroxy Compounds in Autoxidizing Linseed Oil*, Journal of the American Chemical Society, 71 (1949), p. 812-816.

<sup>152</sup> NICHOLLS, R.V.V., HOFFMAN, W.H., *An Infrared Spectrophotometric Investigation of the Autoxidation of Drying Oil Films*, Official Digest, 327 (1952), p. 245-260.

O'Neil,<sup>153</sup> Helme *et al.*<sup>154</sup> and Wilska *et al.*<sup>155</sup>. The painting materials have been analysed by infrared spectroscopy, amongst others, by Van't Hul-Ehrnreich,<sup>156</sup> Low *et al.*<sup>157</sup> and Meilunas *et al.*<sup>158</sup>. Another relatively easy technique of separating the fatty acids after being transformed in methyl esters is distillation.<sup>159</sup> Lastly, differential scanning calorimetry (DSC) has also been used to study the autoxidative curing process of linseed oil catalysed by metal driers.<sup>160</sup>

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<sup>153</sup> O'NEIL, L.A., *Applications of Infra-red Spectroscopy to the Study of the Drying and Yellowing of Oil Films*, Paint Technology, 27 (1963), p. 44-47 and AHLERS, N.H.E., O'NEIL, L.A., *The Structure of Oils and Resins: Spectroscopy*, Journal of Oil and Colour Chemists' Association, 37 (1954), p. 533-561.

<sup>154</sup> HELME, J.P., MOLINES, J., *Étude de l' Isomérisation cis-trans par Spectrophotométrie Infra-rouge au Cours de la Polymérisation de l' Huile de Lin: Application aux Resines Alkydes et Huiles Modifiées*, Revue Française des Corps Gras, 4 (1957), p. 189-202 and *Spectrophotométrie Infra-rouge de l' Huile de Lin: Autoxydation Comparée des Formes cis et trans Dans le Cas d' une Seule Double Liaison*, Oléagineux, 13 (1958), p. 141-148.

<sup>155</sup> WILSKA, S., LAHTINEN, T., *Infrared Spectrophotometric Studies of the Drying Mechanism of Paints: Pigment-Drier Interaction in a Model System*, FATIPEC Congress, 12 (1974), p. 503-509.

<sup>156</sup> VANT HUL-EHRNREICH, E.H., *Infrared Microspectroscopy for the Analysis of Old Painting Materials*, Studies in Conservation, 15 (1970), p. 175-182.

<sup>157</sup> LOW, M.J.D., BAER, N. S., *Application of Infrared Fourier Transform Spectroscopy to Problems in Conservation I. General Principles*, Studies in Conservation, 22 (1977), p. 116-128 and LOW, M.J.D., VARLASHKIN, P.G., *Application of Infrared Fourier Transform Spectroscopy to Problems in Conservation II. Photothermal Beam Deflection*, Studies in Conservation, 31 (1986), p. 77-82.

<sup>158</sup> MEILUNAS, R.J., BENTSEN, J.G., STEINBERG, A., *Analysis of Aged Paint Binders by FTIR Spectroscopy*, Studies in Conservation, 35 (1990), p. 33-51.

<sup>159</sup> GOODWIN, S. R., NEWSHAM, D.M.T., *Kinetics of Decomposition of Methyl Linoleate and Vapor-Liquid Equilibria in Mixtures of Methyl Palmitate and Methyl Linoleate*, Journal of Chemical and Engineering Data, 20 (1975), p. 180-181.

<sup>160</sup> TUMAN, S.J., CHAMBERLAIN, D., SCHOLSKY, K.M., SOUCEK, M.D., *Differential Scanning Calorimetry Study of Linseed Oil Cured with Metal Catalysts*, Progress in Organic Coatings, 28 (1996), p. 251-258.

**AN INVESTIGATION OF THE MATERIALS  
USED IN MORDANTS OF BYZANTINE AND  
POST-BYZANTINE ICONS AND WALL  
PAINTINGS**

## **A. Experiments on the Effect of Different Methods of Pre-Treatment on Linseed Oil**

The preparation of historic art materials is a well-known method that facilitates a better appreciation of historic art techniques and the relation between written sources and the works of art in reality. Furthermore, prepared materials that follow the traditional construction of art objects, both unaged and artificially aged, can be subjected to scientific analysis parallel to the analysis of samples from historic art objects themselves. In the present study prepared oil-mordants were used not only as reference samples to be analysed and compared with the samples taken from icons and wall paintings, but also gave rise to a more thorough understanding of the nature and chemistry of drying oils, the effect of heating and of pigment-dryers on their properties, their drying and ageing mechanisms and eventually to the clearer conception of the technique of mordant gilding itself.

As indicated in the fourth chapter, of the published results of analysis and the documentary sources consulted, the most commonly found drying oil for mordant gilding in European panel and mural painting was linseed oil and, secondarily, walnut oil. In the majority of cases the oil seems to have been heat-bodied on an open fire to increase its stickiness prior to and/or after its mixture with assorted ground pigments, varnishes and various other ingredients. Sun heating was also occasionally adopted. From the sources consulted, the most frequently encountered pigments are the lead-based, i.e. white lead (basic lead carbonate), red lead, massicot <sup>1</sup> and litharge <sup>2</sup>, while verdigris (basic copper acetate) and ochres also constituted major components. The verdigris and some of the lead pigments could have

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<sup>1</sup> Yellow oxide of lead, an intermediate step in the production of red lead from white lead.

<sup>2</sup> Orange-yellow monoxide of lead, again produced as an intermediate step in the preparation of red lead from white lead.

been added mainly for their dryer action. The yellow and red ochres were probably used to give the mordant a distinct colour that helped to distinguish the areas to be gilded, along with enriching the colour of the gold laid on top. Most of the recipes also refer to a varnish as an ingredient for the preparation of oil-mordants, yet without specifying its exact composition. One of the earliest varnishes that seem to have been adopted by painters, especially in Italy, consisted of cooked linseed oil and pulverised sandarac, although other kinds of drying oils and resins had also been employed, such as walnut oil, mastic, colophony and amber.<sup>3</sup>

Following the information obtained from the documentary sources and the confirmation provided by the published scientific analysis, the first step in the preparation of the reference samples was the heating of linseed oil. At this stage experiments were conducted under different heating conditions of temperature and oxygen concentration, in the presence and absence of dryers, dried in the diffuse daylight and in the dark,<sup>4</sup> unaged and artificially aged, with a view to observing the gradual changes in the physical and chemical properties of the oil during heating, drying and ageing and to approaching the original conditions of preparation of oil-mordants.

Cold-pressed raw linseed oil<sup>5</sup> was heated and heat-blown at temperatures ranging between 130°C and 200°C for periods up to 216 hours (9 days). The temperatures were selected to keep below the limits of the flash and boiling points of linseed oil (222°C and 343°C respectively) and the total time of heating was decided in each individual

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<sup>3</sup> See CENNINI, C., *Il Libro dell'Arte*, a cura di F. Brunello, Neri Pozza Editore, Vicenza (1982), p. 104-105 & 156 and MERRIFIELD, M.P., *Original Treatises on the Arts of Painting*, Vol. I, Dover Publications, New York (1967), p. cclxi-cclxxiv.

<sup>4</sup> The drying was carried out in the conservation studio and therefore, alongside the daylight, the artificial light of the studio should be also taken into consideration.

<sup>5</sup> Raw cold-pressed linseed oil from Sweden purchased from Kremer Pigmente, Germany ([www.kremer-pigmente.de](http://www.kremer-pigmente.de)). It was thought that cold-pressed oil nears the one originally used by painters. The walnut oil, pigments and the resins described in this chapter were also purchased from the same company.

case according to the viscosity acquired by the oil during the heating procedure. The heating apparatus used was a three-necked flask, heated uniformly in a stirring heating mantle and equipped with thermometer, condenser and suction pump to control the temperature, vapours and airflow respectively (See Appendix, Figure 2). Raw linseed oil was also sun-heated during the summer season for twenty days.<sup>6</sup> The heated, heat-blown and sun-heated linseed oil was then painted out in thin layers on microscope slides and left to dry for twenty-five days in daylight and in the dark. The heating procedure (temperature and method of heating) and drying conditions are shown in Table 1.

TABLE 1 – *Heating and Drying of Linseed Oil*

	<b>Sun-Heated</b>	<b>130°C - 150°C</b>		<b>160°C - 180°C</b>		<b>200°C</b>	
		<b>Heated</b>	<b>Heat-blown</b>	<b>Heated</b>	<b>Heat-blown</b>	<b>Heated</b>	<b>Heat-blown</b>
<b>Dried in daylight for twenty-five days</b>	One sample after twenty days of exposure	Fifteen samples (one after 8, 12, 26, 33, 50, 57, 74, 81, 98, 104, 116, 130, 137, 154 and 161 hours of heating)	Seven samples (one every 6 hours, up to 42 hours of heating)	Seven samples (one after 12, 24, 48, 72, 96, 120 and 144 hours of heating)	Three samples (one every 6 hours, up to 18 hours of heating)	Seven samples (one after 24, 48, 72, 144, 168, 192 and 216 hours of heating)	One sample after 6 hours of heating
<b>Dried in the dark for twenty-five days</b>	One sample after twenty days of exposure	One sample after 74 hours of heating	One sample after 6 hours of heating	One sample after 72 hours of heating	One sample after 6 hours of heating	One sample after 72 hours of heating	One sample after 6 hours of heating

The above experiments reinforced the belief that heating linseed oil at 130°C-150°C by blowing air through it results in a product that draws

<sup>6</sup> Sun-heated in Athens, Greece during the months of August and September.



closer to the oil described in the recipes, as far as the physical properties of viscosity and colour are concerned. Based on this observation, 70 ml of raw linseed oil was heat-blown at 130°C for six hours, mixed with 1 gr of white lead to act as a dryer and then continued to be heat-blown for another twenty-four hours. Samples were taken every six hours, painted out on microscope slides and left to dry for twenty-five days in daylight and in the dark. At the end of heating the surplus pigment settled at the bottom of the flask. The same procedure was repeated using verdigris as dryer and another set of samples was left to dry under the same conditions and for the same period of time, as shown in Table 2. Three more samples of raw linseed oil were also painted out and left to dry for the same period of time in daylight and in the dark to be compared with the heat-treated.

TABLE 2 – *Drying of Raw Linseed Oil and Heating and Drying of Linseed Oil with White Lead and Verdigris*

	Raw	130°C - 140°C	
		Heat-blown with white lead	Heat-blown with verdigris
<b>Dried in daylight for twenty-five days</b>	Two samples (one from Sweden and one with deposits)	Four samples (one every 6 hours up to 24 hours of heating)	Four samples (one every 6 hours up to 24 hours of heating)
<b>Dried in the dark for twenty-five days</b>	One sample from Sweden	One sample after 6 hours of heating	One sample after 6 hours of heating

A selection of samples described in Tables 1 and 2 were put in a humid oven for forty days at a temperature of 60°C and relative humidity of 50% for the purpose of accelerating the ageing process. The samples selected were those of the heated linseed oil at 200°C, heat-blown at 160°C-180°C and 130°C-150°C, heat-blown with white lead and verdigris at 130°C-140°C and the raw linseed oil.

During heat bodying the oil gradually acquired a darker colour, a change that occurred more rapidly when air was blown through it. Sun-heating produced an oil that was much clearer than the heat-bodied or the raw. In both cases viscosity increased significantly with time of heating. Moreover, the heat-blown, sun-heated and drier-containing oil films hardened and eventually dried two to three days ahead of the raw and simply heated films. All aged films became darker and harder and eventually underwent shrinkage and became wrinkled.

The composition and the chemical changes occurring during heating in the first group of reference samples were examined by the technique of gas chromatography/mass spectrometry (GC/MS).<sup>7</sup> Analysis was carried out on the dried films of the linseed oil heated at 200°C and 130°C-150°C, heat-blown at 200°C, sun-heated and the raw linseed oil, dried in daylight and in the dark, as well as on the aged films of the oil heated at 200°C.

Mills & White first observed that a differentiation between raw and pre-polymerised drying oils in the dried state can be made by comparing the ratios of the three principal carboxylic-acid methyl esters present in the films, namely the azelate, suberate and the sebacate methyl esters; the raw oil films are expected to have higher ratios of azelate to either of the other two methyl esters than the pre-polymerised oil films. This occurs because of the increase in the proportion of the suberic and sebacic diacids relative to azelaic acid, due to thermal rearrangement of double bonds of drying oils before oxidative polymerisation.<sup>8</sup> The results of the analysis of the films of raw linseed oil and that heated at 200°C and 130°C-150°C, all dried in daylight, are shown in Figures 1-4.

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<sup>7</sup> Details about the technique of methylation of the samples to yield the necessary methyl esters, the gas chromatography apparatus and the method of analysis are described in the following section.

<sup>8</sup> MILLS, J.S., WHITE, R., *Organic Mass Spectrometry of Art Materials: Work in Progress*, National Gallery Technical Bulletin, 6 (1982), p. 7. The authors refer to pre-polymerisation by heat or light in the relative absence of air, which does not completely correspond to the present case.

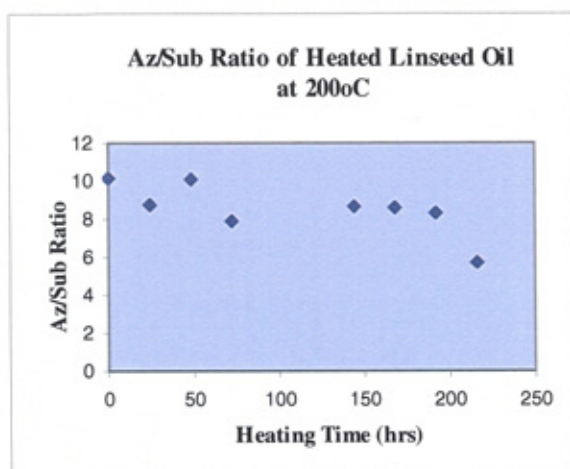


Figure 1

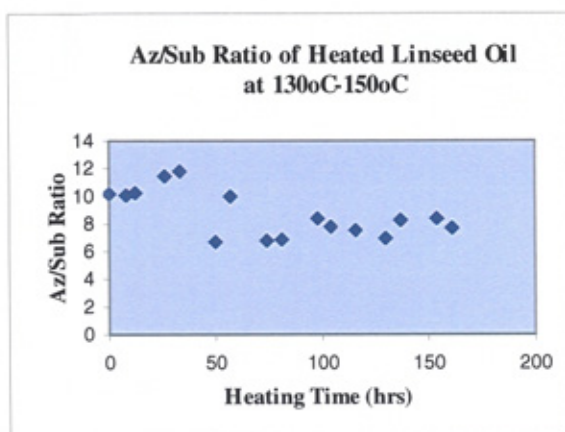


Figure 2

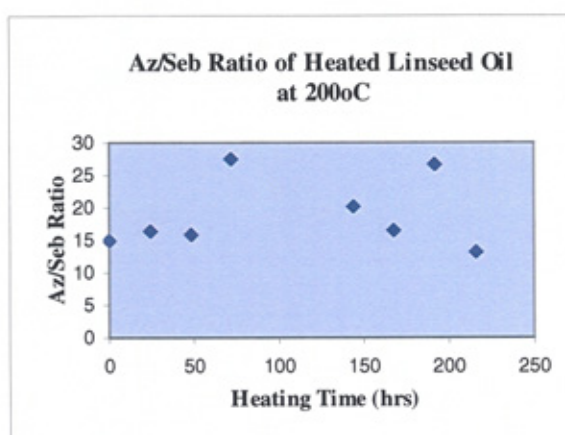


Figure 3

As expected, the values of the azelate to suberate methyl-ester ratio for both temperatures (Figures 1 & 2) show a general decrease from the initial raw to the final heat-bodied oil. However, the azelate to sebacate methyl-ester ratio (Figures 3 & 4) does not present the same decrease and, accordingly, does not correspond to the results quoted by Mills & White. Possible sources of variability in the calculated results are the errors introduced in the work-up procedure of the analysis of the samples (derivitisation and isolation of the fatty acids), switching errors in the GC/MS and errors in measuring the peak areas.

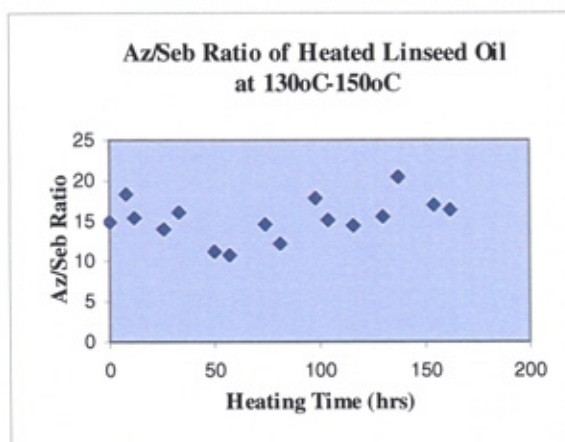


Figure 4

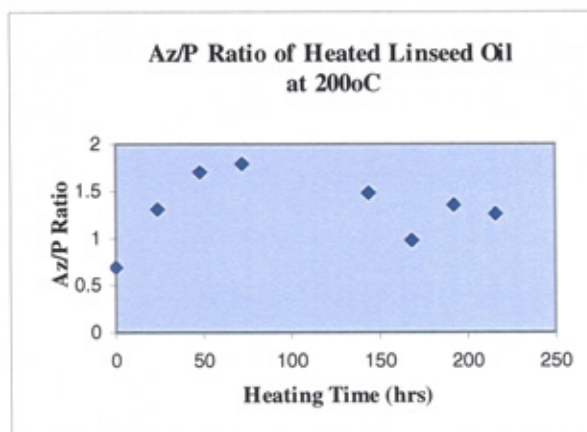


Figure 5

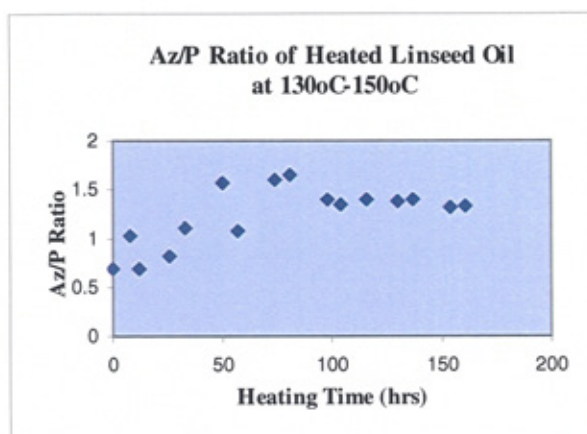


Figure 6

The chromatograms of the raw linseed oil show quite high peaks of oleic acid and low peaks of the three degradation products i.e. the

Some information about the state of a dried-oil film can be extracted from the azelate to palmitate methyl-ester ratio, which is likely to increase during drying and not expected to be affected by heating. A possible explanation is the formation of azelaic acid rather early in the drying period, compared to the formation of the other diacids only after exposure to heat. The results of the analysis of the above-mentioned linseed oil films are shown in Figures 5 & 6 and largely correspond to the small increase expected. The variability in the degree of oxidation of the samples due to varying thickness and, therefore, oxygen concentration in the oil films is another factor that is expected to have influence on this ratio.

azelaic, suberic and the sebacic acids. During heat bodying, however, the dicarboxylic acid peaks grow higher and the oleic acid peak diminishes. It should also be noted that the values of the above mentioned ratios calculated for the sun-heated linseed oil do not present the same changes as in the heat-bodied. The analysis of the heat-blown linseed oil at 200°C did not lead to any meaningful results because of the small number of samples taken. This being the case, there would be little point in presenting them in this context.

The next step was the preparation of reference samples for the purpose of analysing and comparing them with samples taken from icons and wall paintings. The following materials were selected for their preparation, in accordance with the recipes: linseed oil, walnut oil, white lead, verdigris, sandarac and dammar.

Firstly, 200ml of linseed oil and 200ml of walnut oil were heat-blown at 130°C for seventy-two and thirty-six hours respectively. Again the total heating time was decided for each type of oil according to its progressively increased viscosity. Each quantity was divided into four portions of 50ml, to which the following combinations of pigments and resins, 0.5g of each, were added: white lead and sandarac, white lead and dammar, verdigris and sandarac, and verdigris and dammar. The eight different mordants thus produced were heated in a water bath at 100°C for another six hours. They were then painted out on microscope slides and left to dry in the studio for twenty days both in daylight and in the dark. The same eight mordants were aged in the humid oven at 60°C and 50% relative humidity for forty days. The values of the azelate to suberate, azelate to sebacate and the azelate to palmitate methyl-ester ratios of all the above-described samples are presented in Tables 3 & 4.

TABLE 3\* – Azelate to Suberate, Azelate to Sebacate and Azelate to Palmitate Methyl-Ester Ratios of Linseed-Oil Mordants

Type of Film		AZ/SUB	AZ/SEB	AZ/P
<b>Dried in daylight for twenty days</b>	LO+WL+SA	6.44	15.37	0.90
	LO+WL+DA	6.45	~22.25	0.52
	LO+VE+SA	6.20	15.60	1.05
	LO+VE+DA	6.54	~24.33	0.59
<b>Dried in the dark for twenty days</b>	LO+WL+SA	~11.70	~23.40	0.34
	LO+WL+DA	~9.00	~27.00	0.29
	LO+VE+SA	7.36	~31.13	0.78
	LO+VE+DA	6.10	~24.50	0.47
<b>Aged at 60°C and 50% RH for forty days</b>	LO+WL+SA	~3.55	~5.91	0.25
	LO+WL+DA	5.34	13.93	0.68
	LO+VE+SA	4.10	~20.33	0.59
	LO+VE+DA	3.97	24.11	0.66

LO: linseed oil, WL: white lead, VE: verdigris, SA: sandarac, DA: dammar

By comparing the azelate to palmitate methyl-ester ratio values of the linseed oil films presented in the first four rows of Table 3 with those featured in Figure 6, it appears that the former have almost all dropped below zero. In contrast, the latter are almost constantly maintained above zero. Such change can possibly be attributed to the nature of the pigments present in the mordant films, as heating does not seem to significantly affect this ratio.

\* Entries preceded by ~ in both tables have not been calculated with precision because of the low peaks of the azelate and suberate esters and, consequently, the small peak areas.

TABLE 4\* – Azelate to Suberate, Azelate to Sebacate and Azelate to Palmitate Methyl-Ester Ratios of Walnut-Oil Mordants

Type of Film		AZ/SUB	AZ/SEB	AZ/P
<b>Dried in daylight for twenty days</b>	WO+WL+SA	6.78	~23.36	0.53
	WO+WL+DA	5.86	~29.60	0.31
	WO+VE+SA	~10.00	~35.00	0.28
	WO+VE+DA	6.52	~28.25	0.67
<b>Dried in the dark for twenty days</b>	WO+WL+SA	5.88	~26.66	0.45
	WO+WL+DA	3.97	15.31	0.54
	WO+VE+SA	3.17	19.25	0.64
	WO+VE+DA	4.15	18.80	0.64
<b>Aged at 60°C and 50% RH for forty days</b>	WO+WL+SA	4.21	~20.00	0.48
	WO+WL+DA	~2.68	~5.58	0.46
	WO+VE+SA	4.65	44.89	0.51
	WO+VE+DA	3.74	~27.50	0.45

WO: walnut oil, WL: white lead, VE: verdigris, SA: sandarac, DA: dammar

The same observation can be made on the results from the walnut oil films of the first four rows in Table 4 when compared with those presented by Mills from his experiments with unpigmented films (laboratory conditions).<sup>9</sup> Although Mills used walnut oil that had not been heat-bodied in films pigmented with white lead and verdigris whose azelate to palmitate methyl-ester ratios are above zero, they are still lower than those of his unpigmented films. Accordingly, the below

<sup>9</sup> See MILLS, J.S., *The Gas Chromatographic Examination of Paint Media: Part I. Fatty Acid Composition and Identification of Dried Oil Films*, *Studies in Conservation*, 11 (1966), p. 103, Table III.

zero values of this ratio seen in Table 4 might be an indication of the presence of those two pigments in the oil films in question. Furthermore, the values of the aged films for both oils were expected to slightly increase with ageing due to the formation of azelaic acid, instead of remaining stable.



## **B. Analysis of Samples Taken from Icons and Wall Paintings**

In order to give evidence to support the documentary sources and the findings from the few published works on oil-mordant gilding, analysis needed to be carried out on samples taken from mordant-gilded areas of icons and wall paintings. To this end, a total of twenty samples, fourteen from wall paintings and six from an icon, were examined by means of staining tests on cross-sections and the techniques of gas chromatography/mass spectrometry (GC/MS) and scanning electron microscopy-energy dispersive X-Ray (SEM-EDX).

The wall paintings sampled derive from the main churches of two monasteries situated in Thessalia, Central Greece; the main church of the Transfiguration Monastery at the monastic community of Meteora, painted in 1552 A.D., and the main church of the St. Byssarionas Monastery at Doussiko, painted in 1557 A.D. by the iconographer *Tzortzis*. The single private icon sampled hails from the Post-Byzantine period, possibly the eighteenth century, and depicts St. Spyridonas. The main reason for sampling from a number of wall paintings and only one icon is that the considerable thickness of the mordant layer on murals facilitates the detection of any possible trace of oil, in contrast to the very thin and difficult to analyse mordant layer found on icons. The paintings, however, may have been restored more than once and, therefore, the samples are likely to contain some contaminants.<sup>10</sup>

In general, samples were taken from damaged areas and cracks of the paintings to avoid disfiguring the pictorial surface. As already mentioned, the mordant-gilding technique was employed in Byzantine mural painting for all gilded decoration. Thus, mural samples were taken from both the haloes of the saints and the linear embellishments of their cloaks and mantles, i.e. hems and floral or other decorative

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<sup>10</sup> The mural painting decoration of the main church of St. Byssarionas Monastery was restored in 1985, while certain areas of the icon sampled have been extensively repainted.

motifs. Some of the scenes and the areas of the wall paintings sampled are shown in Plates 1-7 and all are described in Table 5 (S<sub>1</sub>-S<sub>14</sub>). The size of these samples was sufficient for both the preparation of cross-sections needed for the staining tests and the SEM-EDX microanalysis and for the GC/MS analysis. The areas of the icon to be sampled were firstly carefully cleaned of varnish with ammonia, while different samples were taken for use with each analytical method and technique, as shown in Plate 8 and Table 5 (S<sub>16</sub>-S<sub>18</sub>). Three extra samples were taken, two that had not been cleaned of varnish (S<sub>15</sub> and S<sub>19</sub>) and one from the water-gilded background of the icon (S<sub>20</sub>), both to be compared with the other mordant-gilding samples.

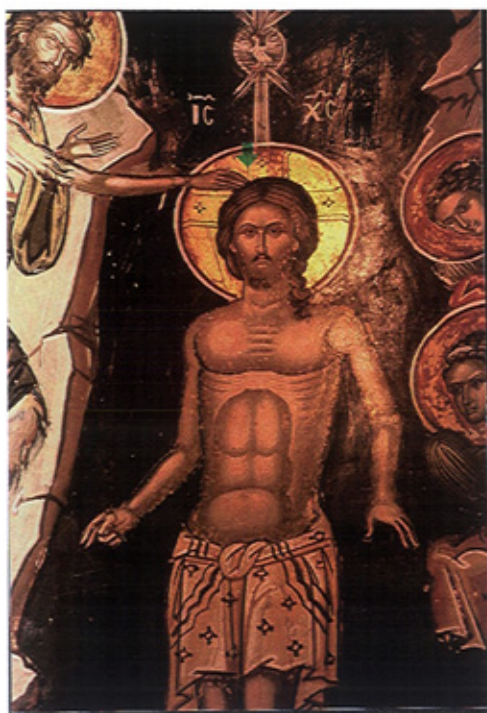


Plate 1 – Christ  
*The Baptism – Main Church of  
the Transfiguration Monastery –  
 Meteora*



Plate 2 – St. John the Baptist  
*The Baptism – Main Church of  
the Transfiguration Monastery –  
 Meteora*



Plate 3 – St. Demetrios  
Detail of decorative motif of red  
cloak – Main Church of the  
Transfiguration Monastery –  
Meteora

Plate 4 – St. Demetrios  
Main Church of the  
Transfiguration Monastery –  
Meteora





Plate 5 – St. Artemios  
Main Church of the  
Transfiguration Monastery –  
 Meteora



Plate 6 – St. George  
Main Church of the  
Transfiguration Monastery –  
 Meteora



Plate 7 – St. Demetrios  
Main Church of the St.  
Byssarionas Monastery –  
Doussiko



Plate 8 - St. Spyridonas

Staining is a technical method used as the first step in the identification of proteins and lipids in the cross-sections of paint samples. In the present study it was used to detect oil in the mordant-gilding samples, which would then provide confirmation of the use of oil-mordants in Byzantine icon and mural painting. The samples for cross-sections were mounted in transparent polyester resin, ground and polished to reveal their stratigraphy. The stain chosen for the detection of oil was Sudan Black B.<sup>11</sup> A drop of the solution was placed on each

<sup>11</sup> The solution used was made up in 70% aqueous ethanol.

cross-section, left for twenty minutes and then rinsed with 50% aqueous ethanol and washed with distilled water. The cross-sections were observed and photographed both before and after staining under a James Swift polarising light microscope Modl MP3500M (BL) equipped with ultraviolet light source and an automatic photography device Nikon Labphot-2. The results obtained are shown in Table 5 and the more representative of the cross-sections photographed in polarised visible light and ultra-violet radiation are shown in Table 6.

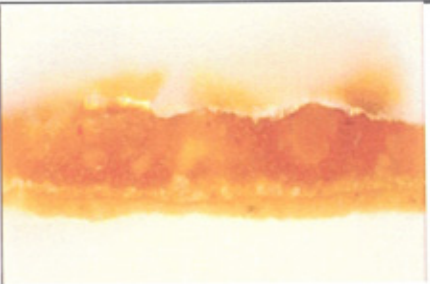

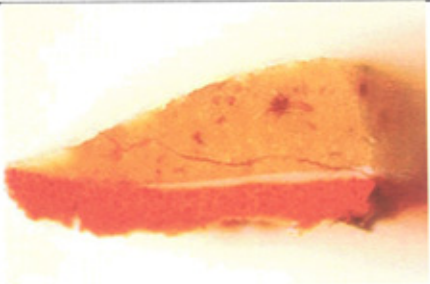


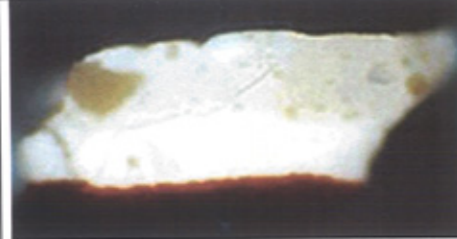



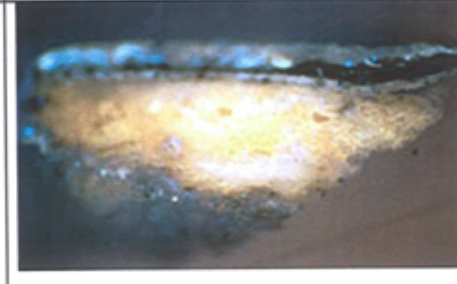
The staining results required support from other analytical methods. To identify the drying oils and resins gas chromatography/mass spectrometry (GC/MS) was carried out using a Hewlett Packard 5890 series III gas chromatographer fitted in a Hewlett Packard 5971A mass selective detector. The samples were used as such without isolation of specific mordant layers. They were derivatised in small Pierce reacti-vials using TMTFTH [3-(trifluoromethyl)phenyltrimethylammonium hydroxide], heated at a temperature of 60°C for six hours. Fatty-acid methyl esters were separated on a 25m×0.53mm methyl silicone capillary column with HT1 bonded phase. The oven temperature programme was set at 35°C for 0.5min, then increasing at 25°C/min to 120°C, followed by a one-minute isothermal period and then increasing again at 7°C/min to 290°C. Helium carrier gas was pressure-controlled to give an MS source pressure of  $1 \times 10^{-5}$  Torr at the initial column temperature of 35°C. The MS operated in positive EI (electron impact) mode at 70eV; source temperature 300°C; scan mode, 600-40 amu (atomic mass units); 0.9s scan time; 0.1s reset time.



TABLE 5 – Description of Samples and Results of Staining Tests Using Sudan Black B as Stain for Oil

SAMPLE CODE	DESCRIPTION	STAINING RESULTS
S <sub>1</sub>	Christ's halo	Stained sporadically
S <sub>2</sub>	St. John the Baptist's halo	Stained sporadically
S <sub>3</sub>	Paint layer underneath St. John the Baptist's halo gilding	—
S <sub>4</sub>	Decorative motif on St. Demetrios's red cloak (Meteora)	Stained uniformly with black spots
S <sub>5</sub>	"	Stained sporadically
S <sub>6</sub>	Hem of St. Artemios's white mantle	Not stained
S <sub>7</sub>	"	Stained below gold leaf and sporadically
S <sub>8</sub>	Decoration on hem of St. George's mauve cloak	Stained below gold leaf
S <sub>9</sub>	Decorative motif on St. George's mauve cloak	Not stained
S <sub>10</sub>	Decoration on hem of St. George's mauve cloak	Stained sporadically
S <sub>11</sub>	St. Paul the Thebian's halo	Stained sporadically
S <sub>12</sub>	St. Cosmas the Poet's halo	Not stained
S <sub>13</sub>	Decorative motif on St. Demetrios's red cloak (Doussiko)	Stained sporadically
S <sub>14</sub>	Decorative motif on St. Ermogenis's cloak	Not stained
S <sub>15</sub>	Decorative black cross on St. Spyridonas's white stole	—
S <sub>16</sub>	"	—
S <sub>17</sub>	"	Not discernible Paint layer stained
S <sub>18</sub>	Decoration on St. Spyridonas's book	—
S <sub>20</sub>	Background	—

TABLE 6 – Examples of Cross-Sections in Visible Light and Ultra-Violet Radiation (Magnification 200x)

SAMPLE CODE	VISIBLE	ULTRA-VIOLET (UV)
S <sub>1</sub>		
S <sub>5</sub>		
S <sub>13</sub>		
S <sub>14</sub>		
S <sub>17</sub>		



As previously explained, during drying and ageing of oil films, cross-linking and photo-oxidation reactions occur, resulting in the reduction of the amounts of unsaturated fatty acids. Yet saturated acids, being less reactive, remain in the film. Due to their relative stability, they have been utilised as internal standards in studies of oil paints. It has been observed that the ratio of the amounts of the two adjacent saturated acid methyl esters, palmitate and stearate, remains fairly constant for the same oil and differs for different oils. Accordingly, the palmitate and stearate methyl-ester ratio can constitute an identifying feature of the drying oil present in a paint film. The azelate to palmitate ratio may confirm the presence of a drying oil in the film while the azelate to suberate and azelate to sebacate ratios are indicative of whether the oil has been pre-polymerised or not.<sup>12</sup> The palmitate to stearate, azelate to suberate, azelate to sebacate and azelate to palmitate methyl-ester ratios of the analysed samples and the conclusions drawn are shown in Table 7.

The results obtained by the staining tests and the GC/MS analysis were supplemented with analysis carried out using scanning electron microscopy-energy dispersive X-Ray (SEM-EDX). This technique led to the detection of the presence of metal ions, such as lead and copper, which constitute the main compounds of certain pigments with dryer action, in the samples. The equipment used was a scanning electron microscope with electron microprobe Hitachi type S-240, MFG N°14-10 and the samples examined were first mounted on aluminium stubs and coated in carbon. The metals detected in those of the samples that were analysed are presented in Table 8 and a number of them are included in Figures 7-10.

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<sup>12</sup> MILLS, J.S., *The Gas Chromatographic Examination of Paint Media: Part I. Fatty Acid Composition and Identification of Dried Oil Films*, *Studies in Conservation*, 11 (1966), p. 97 & 103-106.

TABLE 7\* – Palmitate to Stearate, Azelate to Suberate, Azelate to Sebacate and Azelate to Palmitate Methyl-Ester Ratios of Samples

SAMPLE CODE	P/S	AZ/SUB	AZ/SEB	AZ/P	CONCLUSIONS
S <sub>1</sub>	~2.00	~0.85	~1.30	~0.75	Pre-polymerised Linseed Oil - No Resin
S <sub>2</sub>	1.50	2.00	5.95	0.56	Pre-polymerised Linseed Oil - No Resin
S <sub>3</sub>	—	—	—	—	No Oil - No Resin
S <sub>4</sub>	~4.33	~2.10	~6.02	1.03	Pre-polymerised Walnut or Poppyseed Oil - No Resin
S <sub>5</sub>	1.68	1.83	9.63	0.47	Linseed Oil - No Resin
S <sub>6</sub>	1.43	1.76	5.23	0.58	Pre-polymerised Linseed Oil - No Resin
S <sub>7</sub>	~3.50	~0.66	~1.81	~1.17	No Oil or slight trace
S <sub>8</sub>	~4.95	~1.16	~2.98	~0.32	No Oil or slight trace
S <sub>9</sub>	1.53	1.85	5.79	0.51	Pre-polymerised Linseed Oil - No Resin
S <sub>10</sub>	4.21	~1.89	~7.33	0.11	Walnut Oil or Animal Fat or Egg - No Resin
S <sub>11</sub>	~3.08	~1.15	~5.36	~0.42	No Oil or slight trace
S <sub>12</sub>	—	—	—	—	No Oil
S <sub>13</sub>	2.65	2.30	4.92	0.41	Pre-polymerised Walnut Oil - No Resin
S <sub>14</sub>	7.69	3.26	~15.16	0.50	Poppyseed Oil or Animal Fat - No Resin
S <sub>15</sub>	—	—	—	—	No Oil
S <sub>16</sub>	—	—	—	—	No Oil
S <sub>17</sub>	—	—	—	—	—
S <sub>18</sub>	3.41	~3.95	~2.82	0.23	Pre-polymerised Walnut Oil - No Resin
S <sub>20</sub>	1.81	~4.88	~10.52	0.30	Linseed Oil - No Resin

\* For entries with dash, one or both of the fatty acid in the appropriate ratio were measured by peak height instead of peak area.

TABLE 8 – Results of SEM-EDX Analysis

S <sub>1</sub>	S <sub>5</sub>	S <sub>11</sub>	S <sub>14</sub>	S <sub>17</sub>	S <sub>18</sub>
Lead (Pb) Iron (Fe)	Lead (Pb)	Lead (Pb)	Lead (Pb) Copper (Cu) Iron (Fe) Aluminium (Al) Silica (Si)	Lead (Pb) Silica (Si)	Lead (Pb) Copper (Cu) Iron (Fe) Aluminium (Al) Silica (Si) Gold (Au)

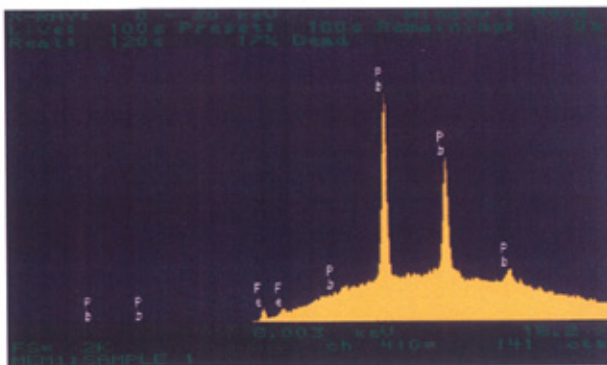


Figure 7 – SEM-EDX of S<sub>1</sub>

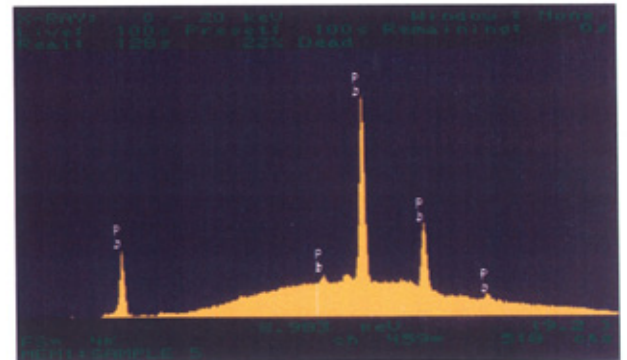


Figure 8 – SEM-EDX of S<sub>5</sub>

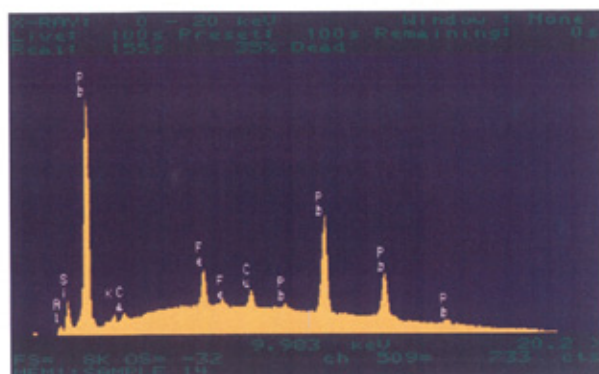


Figure 9 – SEM-EDX of S<sub>14</sub>

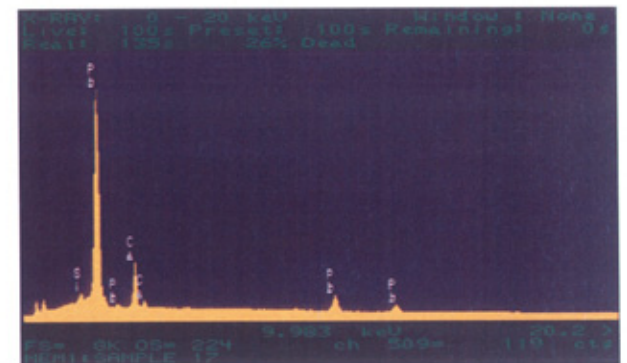


Figure 10 – SEM-EDX of S<sub>17</sub>

### **C. Discussion, Conclusions and Future Work**

The object of this final section is to give some account of how the results obtained by the staining tests and the analytical methods can contribute to the identification of the materials used in the mordants of the icon and wall-painting samples. It will also explain how the knowledge of the composition of the various classes of materials covered in previous chapters has been arrived at.

By observing the cross-sections of the wall-painting samples under the microscope, it becomes evident that they all consist of a distinct, predominantly thick, golden-brown layer below the gold leaf that contains pigment particles of various sizes. This appears to be the mordant layer and although no specific analysis has been carried out to identify the pigments contained, ochre seems to have been the one mostly used. Other pigments can also be discerned, for instance a red pigment can be observed in many of them, a black pigment in  $S_{11}$  and a blue pigment in  $S_{14}$ . In the case of the samples taken from embellishments of garments, a white-coloured layer is seen beneath the mordant and the paint layer below it seems to correspond to the cloak or mantle of the saint (Table 6,  $S_5$ ,  $S_{13}$ ,  $S_{14}$ ). In the samples taken from haloes, the mid-golden layer below the mordant appears to play the role of the “bole” to the gold leaf (Table 6,  $S_1$ ). The staining tests suggest that in the majority of cases the mordant layer contains oil mixed with other components. Some samples are characterised by a strongly stained layer just below the gold leaf ( $S_7$ ,  $S_8$ ); this may be indicative of a high concentration of oil in that area. Nevertheless, these results could not lead to reliable conclusions about the composition and the presence or lack of oil in this layer.

As far as the icon is concerned, the staining tests did not offer any meaningful results. The mordant layer between the gold leaf and the

successive black and white paint layers corresponding to the black decorative cross on the white stole of the saint is so thin that its composition cannot be discerned. However, the thick golden-coloured paint layer underneath has been stained, revealing the possible use of oil as medium for the painting of the cloak (Table 6, S<sub>17</sub>).

The conclusions regarding the GC/MS analysis of the unknown samples were based on the comparison of their palmitate to stearate methyl-ester ratio values with those of the reference samples and those found in the literature. The P/S of the reference samples ranged between 1.40 and 3.28 for the linseed oil and between 2.89 and 8.82 for the walnut. Considering that the same sample of oil was involved in each case, the spread in results must represent imprecision resulting from the work-up and analytical method rather than a real variation in composition. The literature values for linseed oil give an average ratio of 1.5, whereas the ratio is 2.5 for walnut oil and 5 for poppy-seed oil. The more representative of the chromatograms of both the reference and the unknown samples are shown in the Appendix, Figures 3-11.

Of the three main kinds of drying oils used in European painting, linseed oil was the one more frequently detected in the samples analysed. Because the ratio of walnut oil falls between the ratios of linseed and poppy, and the walnut and poppy overlap, it is not always possible to differentiate between the latter two oils. Furthermore, the possibility of differentiation of mixtures of the three oils based solely on P/S ratio is relatively low.<sup>13</sup> The Az/P ratio yet again presents values that in some cases are far below zero, thus opposing the values quoted in the literature as being greater than 1 and also indicating the possible

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<sup>13</sup> SCHILLING, M.R., KHANJIAN, H.P., *Gas Chromatographic Determination of the Fatty Acid and Glycerol Content of Lipids: I. The Effects of Pigments and Aging on the Composition of Oil Paints*, in *ICOM Committee for Conservation, 11th Triennial Meeting in Edinburgh, Scotland, 1-6 September 1996: Preprints*, edited by J. Bridgland, Vol. I, James & James, London (1996), p. 222.

presence of egg ( $S_{10}$  and  $S_{19}$ ).<sup>14</sup> Moreover, with many of the Az/Sub ratios being around 2 and Az/Seb ratios around 4, there are indications that in those cases the oil has been pre-polymerised, in contrast to the combination 7 and 25 of these ratios suggesting that the oil in question has not been pre-polymerised.<sup>15</sup> From the reference samples quoted in Tables 3 & 4 only the aged films that contain linseed oil, white lead and sandarac and walnut oil, white lead and dammar correspond to those literature values.

As far as the resins are concerned, there are no clear indications that may suggest their presence in the samples examined. In the case of two samples ( $S_{10}$  and  $S_{14}$ ) palmitoleic acid was detected, an acid that is associated with animal fats. However, its detection as a result of the presence of finger oil from people touching those wall paintings cannot be ruled out. The quantity of organic material being studied in these samples is so small that results can be greatly distorted by even traces of other substances. For this reason, a blank sequence without a sample has been run to check on background levels. Moreover, due to the difficulty of isolating the mordant layer for the GC/MS analysis, the samples may have been contaminated with adjacent paint layers. The oleic-acid methyl ester is also present in some chromatograms, suggesting that the oil has not yet completed its drying process<sup>16</sup> and the amount of this acid present in a film is also dependant on the pigment present<sup>17</sup>. The high proportion of the azelate methyl ester in almost all chromatograms provides evidence for the presence of degradation products in the films. For samples with the remark “no oil” or “slight trace”, very low or no peaks at all appeared in the chromatograms, suggesting that either the samples contain no oil, the

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<sup>14</sup> MILLS, J.S., WHITE, R., *The Organic Chemistry of Museum Objects*, Butterworth-Heinemann, 2<sup>nd</sup> Edition, Oxford (1999), p. 171.

<sup>15</sup> MILLS, J.S., WHITE, R., *Organic Mass Spectrometry of Art Materials: Work in Progress*, National Gallery Technical Bulletin, 6 (1982), p. 7

<sup>16</sup> See Appendix, Figure 11.

<sup>17</sup> MILLS, J.S., WHITE, R., *The Organic Chemistry of Museum Objects*, Butterworth-Heinemann, 2<sup>nd</sup> Edition, Oxford (1999), p. 171.

concentration of the oil in the mordant layer is too low or that the mordant layer is too thin to provide evidence of the materials it contains. Similarly, the possibility of the use of different types of mordants containing substances other than oil cannot be excluded.

Additives that catalyse oxidation, such as pigments that act as dryers, have little effect on the relative amounts of diacids and, therefore, cannot be detected by the ratios of the diacids-methyl esters. The results obtained by the SEM-EDX analysis reveal that all the samples analysed contain lead in the mordant layer. This is indicative of the use of lead pigments in that layer, such as white lead and red lead, whose main role is their dryer action.<sup>18</sup> The metal ions of copper and iron have also been detected in some of them, suggesting the presence of copper- and iron-based pigments, such as verdigris and ochres.

It appears, therefore, that the findings of the present study seem to largely agree with the documentary sources and the previous studies on the oil-mordants cited in the fourth chapter. The wall-painting samples analysed are not representative of both the Byzantine and Post-Byzantine eras. Nevertheless, they all date from the sixteenth century and can thus provide useful information about the technology applied at this moment in Byzantine art history. The single icon examined can only give indications of the materials that may have been used. The fact that the mordant layer is very thin makes analysis even more difficult. Accordingly, based on this limited study, it appears that the oil-mordants used in Byzantine icon and mural painting correspond with those used at the same time in the West, although the technique for application of gold in murals itself does not accord with the comparative Western technique.

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<sup>18</sup> The use of these pigments for their strong colour effect on the mordant layer cannot be ruled out.

Apart from the results regarding the materials found in mordants, a stylistic observation should be stated in this context. By comparing the cross-sections of the wall-painting samples taken from the two representations of St. Demetrios at Meteora and St. Demetrios at Doussiko, it is evident that their stratigraphy is the same (See Table 6, S<sub>5</sub>, S<sub>13</sub>). A single glance at the two representations (Plates 4 & 7) makes it quite obvious that the saints depicted are exactly the same. It can therefore be suggested that the two paintings have been executed by the same hand. Given the fact that the painter of the main church the St. Byssarionas Monastery at Doussiko has been identified as the iconographer Tzorzis, there is very strong evidence that Tzorzis operated in other monasteries in the general area of Thessalia, including the main church of the Transfiguration Monastery at Meteora.

This study constitutes only the beginning of the investigation of a number issues that have arisen. Although the results obtained may lead to some conclusions, some of them contradict each other, particularly as far as the oil present in the mordant films and identified by the staining tests and the GC/MS analysis is concerned. For instance samples S<sub>6</sub>, S<sub>9</sub> and S<sub>14</sub>, although not stained for oil, gave evidence for the presence of oil in the GC/MS analysis. It is true, however, that staining tests are quite often unreliable and can give falsely negative results since thoroughly dried oil does not adequately absorb stains unless it is heated to about 60°C.<sup>19</sup> It is clear that further analysis should be carried out to enhance the validity of these results, especially using other analytical methods that were not at the disposal in this

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<sup>19</sup> MILLS, J.S., WHITE, R., *The Organic Chemistry of Museum Objects*, Butterworth-Heinemann, 2<sup>nd</sup> Edition, Oxford (1999), p. 177.



study, such as FT-IR spectroscopy.<sup>20</sup> The success of the method of this kind of study depends on obtaining a large number of results and, therefore, more icons and wall paintings ought to be analysed to obtain a more concrete idea of the mordants used. Molar ratios of the previously mentioned fatty acids to the glycerol content of a mordant layer can be also useful to characterise the drying oils contained.

Finally, the topic of the presence of resins in the oil-mordants has not been examined extensively in this thesis. The identification of small amounts of resin in paint media is another problem that has been rather uncertain when relying on gas chromatography alone. Often the identification of unusual or less common minor peaks that appear in gas chromatograms calls for mass spectrometry. This technique has proved to be of particular value in confirming the presence of resin components in samples and a more thorough investigation ought to be carried out in this direction, to supplement the findings of this study.

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<sup>20</sup> Analysis using the technique of DTMS (Direct Temperature Resolved Mass Spectrometry) is currently being carried out. Since this technique is more sensitive than GC/MS, there is a higher probability of detecting any traces of organic material related to oils in the samples where the results to date have been ambiguous.

## **APPENDIX**

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Central Area	Near East	Balkans	Sicily
330 Foundation of Constantinople, the ancient Byzantium, as capital of the Roman world	222		
		Sasanian Dynasty in Persia	
527 – Reign of Justinian I—so-called 'First Golden Age' of Byzantine Culture 565 –			
	632 – 638 – 642 – Islamic conquest of Syria and Egypt 650 –		
	591 Byzantine governors in Armenia	Omayyad Caliphate at Damascus	
726 – Iconoclast Age at Constantinople	705 Establishment of the Abbasid Caliphate at Baghdad	679 –	
843 –		First Bulgarian Empire	
867 –	885		878 – Period of Byzantine domination 909 –
	Macedonian Dynasty at Constantinople— so-called 'Second Golden Age' of Byzantine Culture		
	Bagratid kingdom in Armenia with its capital at Ani		
	1045 – Armenia annexed by Byzantium	1018 –	
1054 Final split between the Catholic and Orthodox Churches		Cyril and Methodius bring Christianity to the Slavs	
1057 – 1071 Battle of Manzikert— defeat of the Byzantines by the Seljuk armies	1080 – 1089 –	1060	1071 Norman Conquest
	Ducas, Comnene and Angelus Dynasties at Constantinople	Byzantine control of Bulgaria	
	Period of Georgian Ascendancy	1169 – 1186 – Beginnings of Serbian independence under Stephen Nemanja	
1204 – Latin Dynasty rules at Constantinople— growth in power of Byzantine rulers at Nicaea 1261 –	1204 – 1220 – Arrival of the Mongols in Western Asia	1186 – Second Bulgarian Empire	
	Comnene Dynasty at Trebizond		
	1375 –	1393 –	
1453 Fall of Constantinople to the Ottoman Turks	1461 –		

Figure 1 – Table of the most significant events of the Byzantine history.

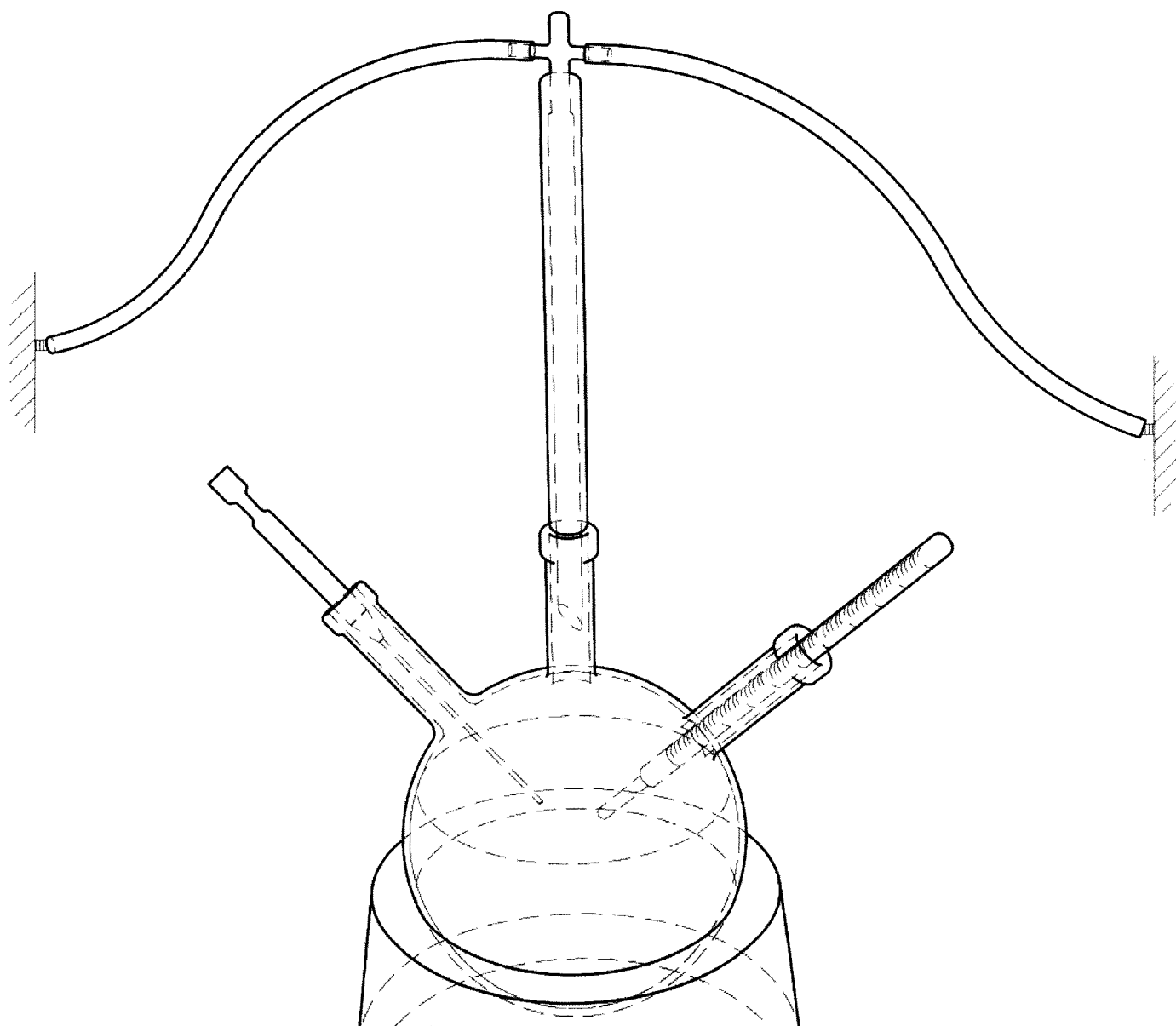


Figure 2 – Heating apparatus for preparation of reference samples.

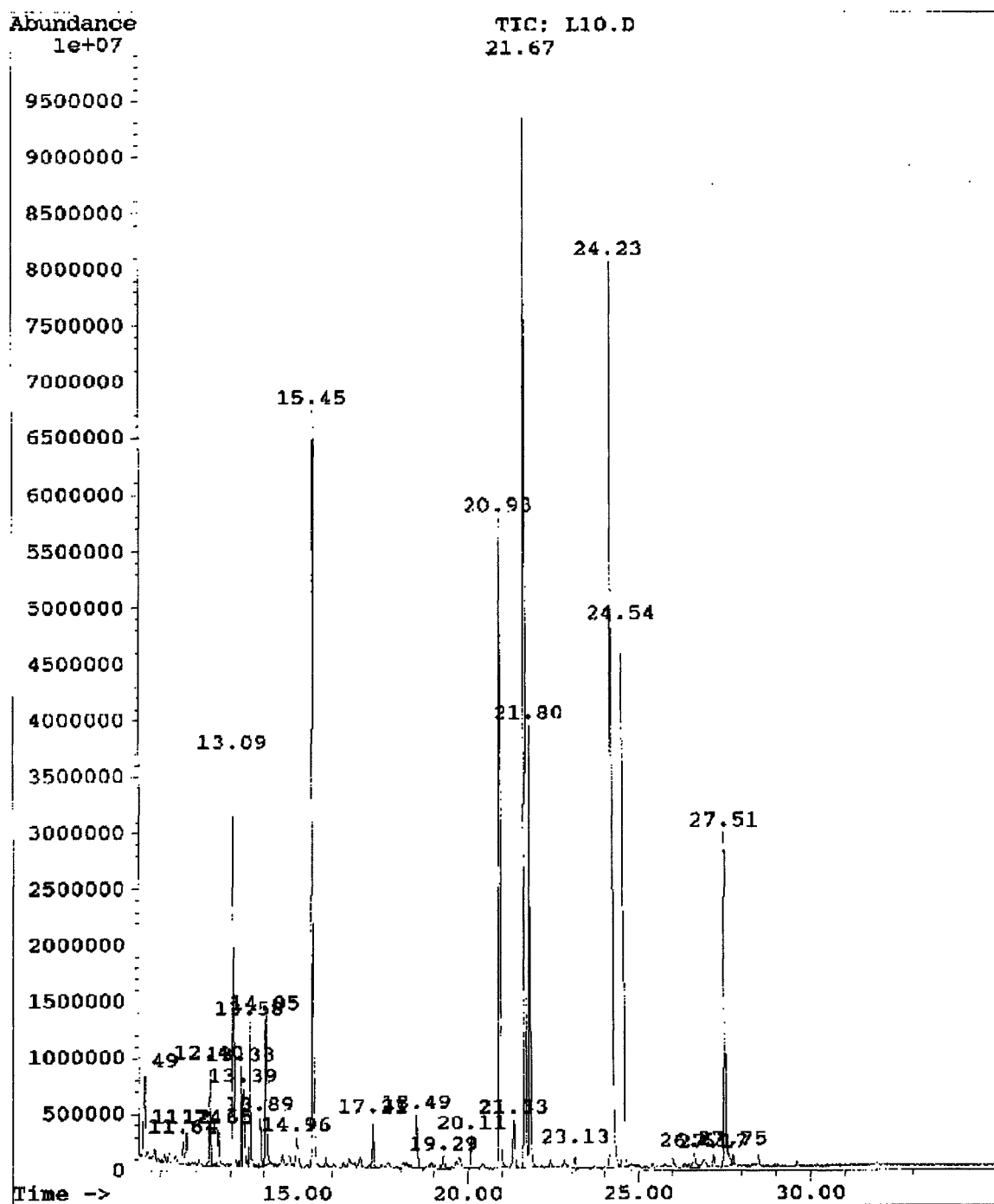


Figure 3 – Chromatogram of the reference sample containing linseed oil, white lead and dammar, aged at 60°C and 50% RH for forty days.

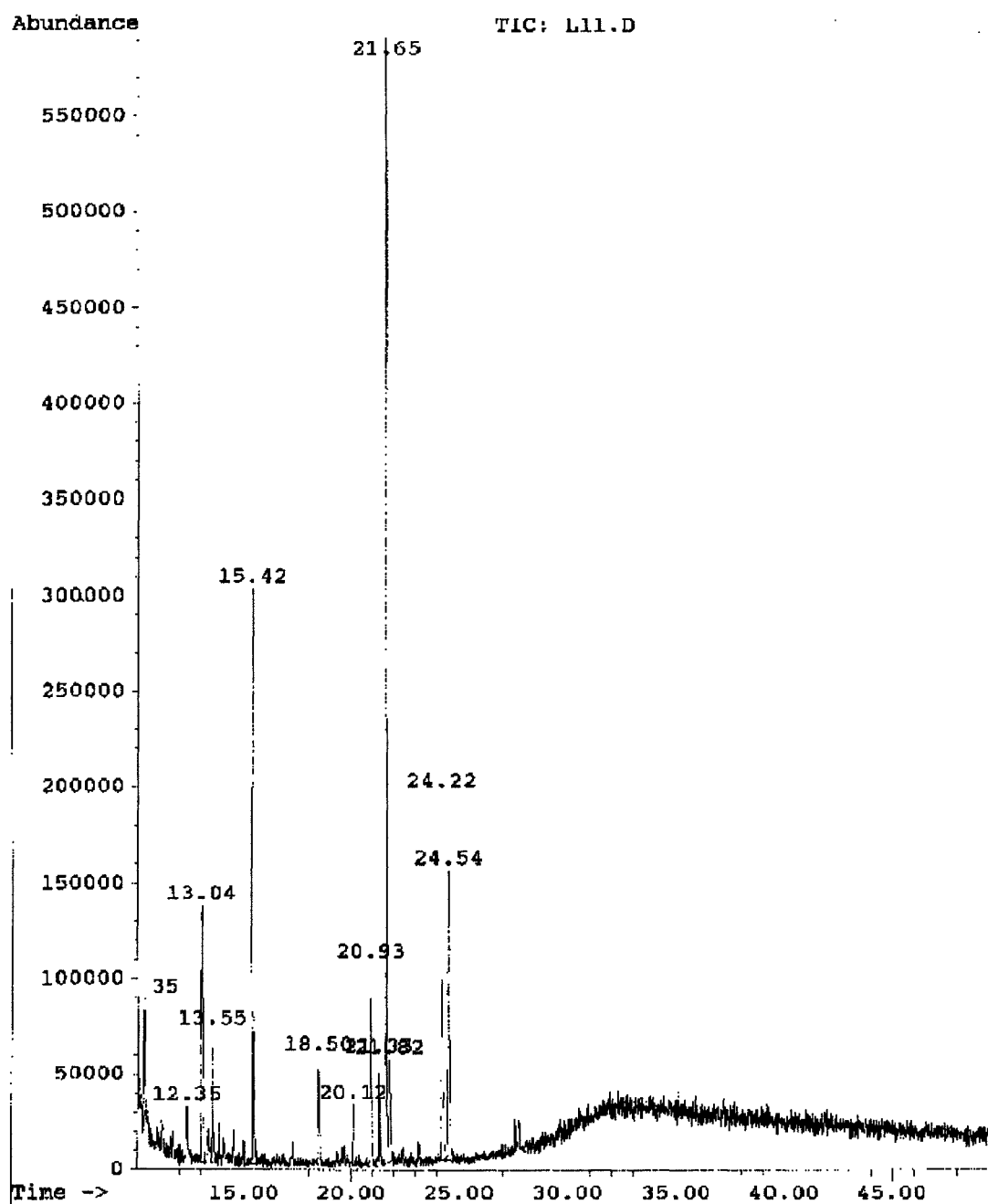


Figure 4 – Chromatogram of the reference sample containing linseed oil, verdigris and sandarac, aged at 60°C and 50% RH for forty days.

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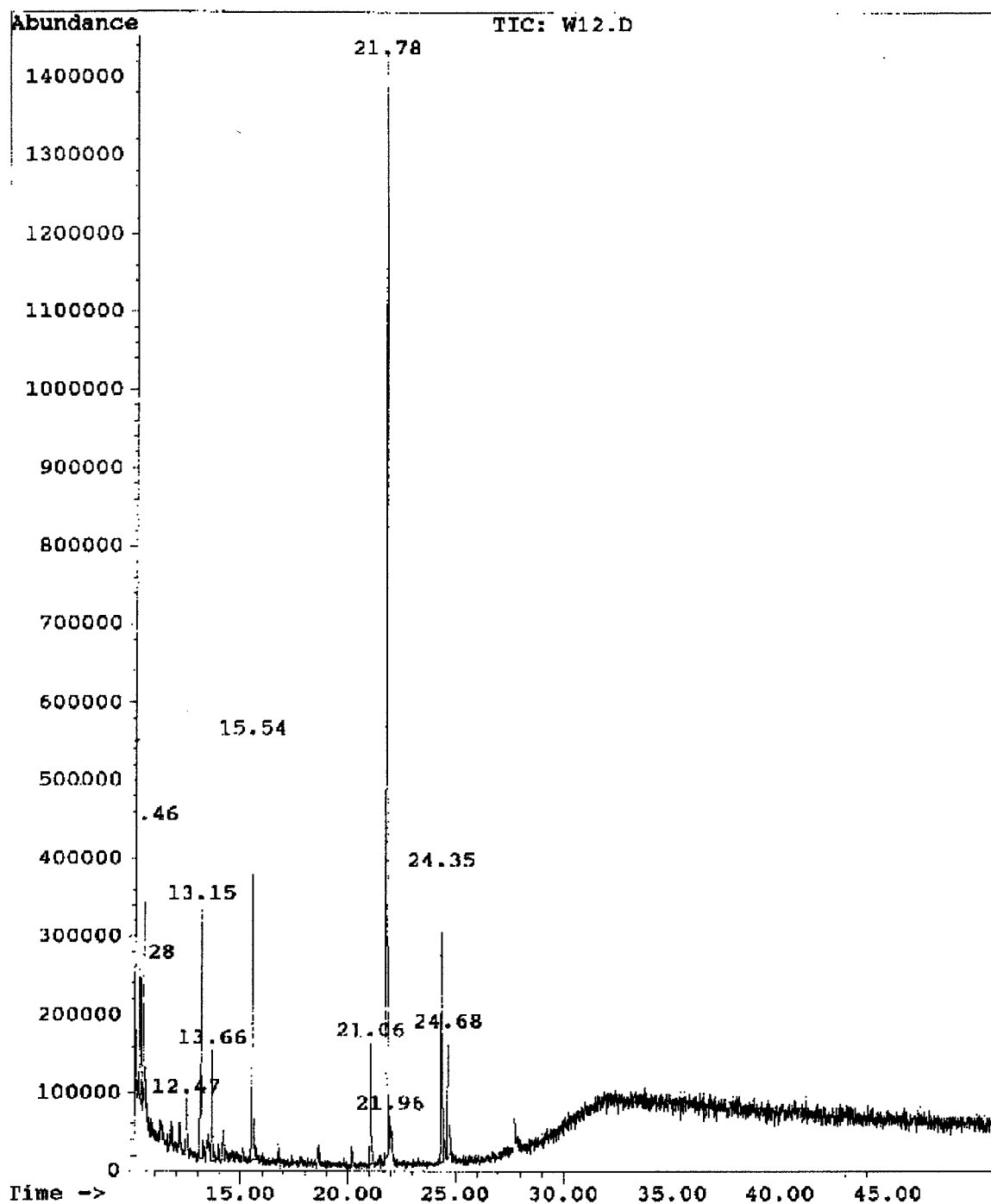


Figure 6 – Chromatogram of the reference sample containing walnut oil, verdigris and dammar, aged at 60°C and 50% RH for forty days.



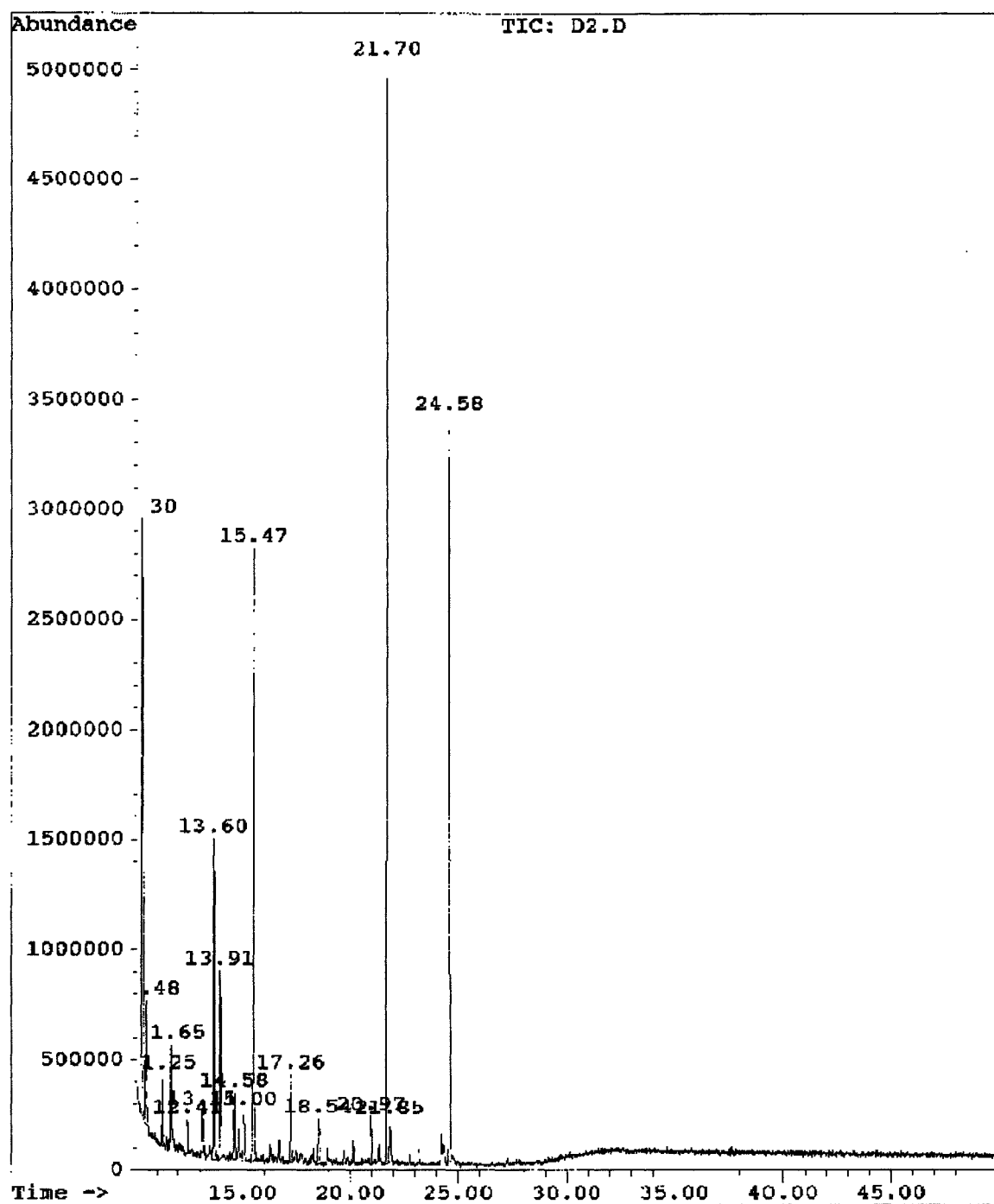


Figure 7 – Chromatogram of the unknown sample S<sub>2</sub>.

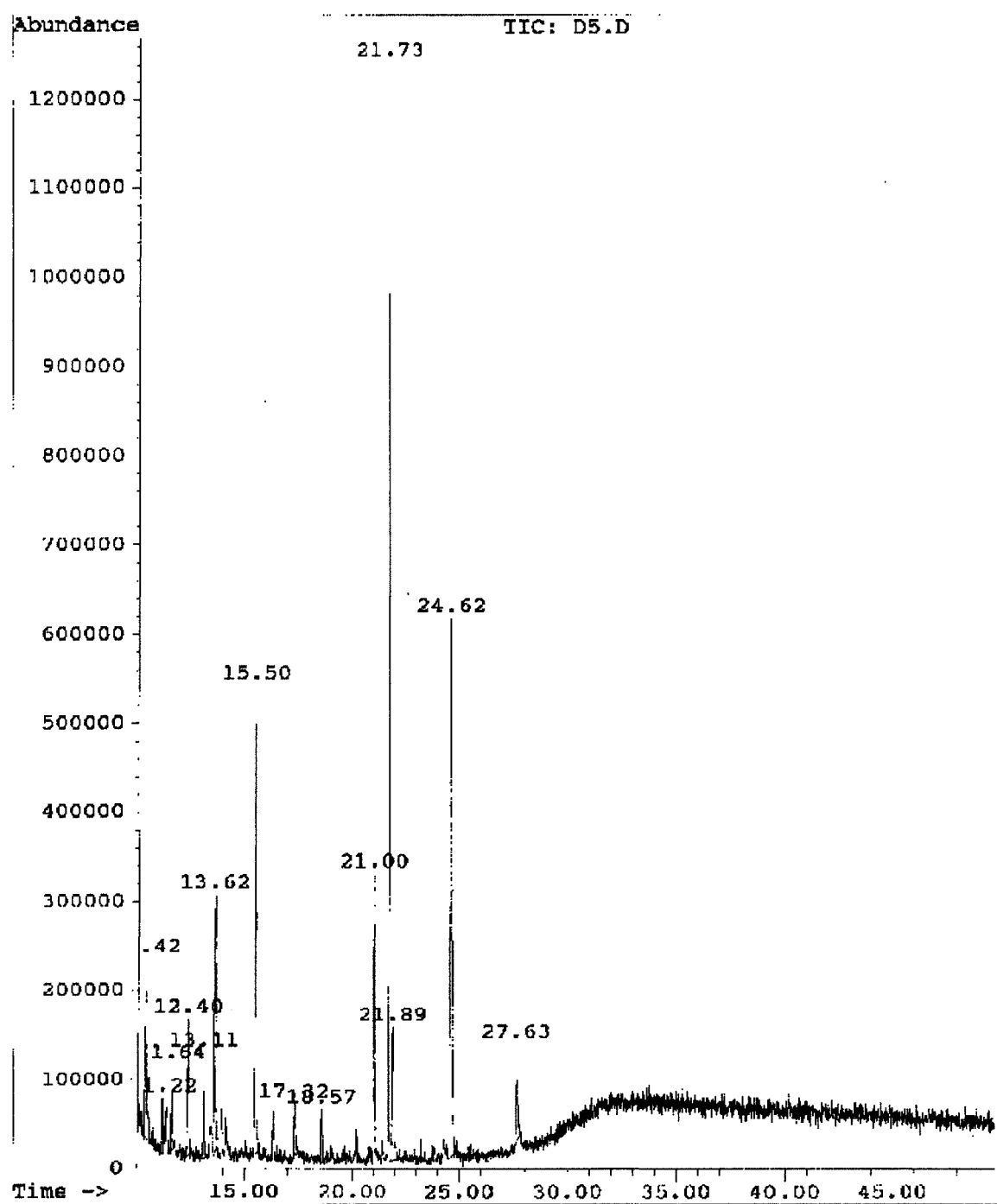


Figure 8 – Chromatogram of the unknown sample S5.

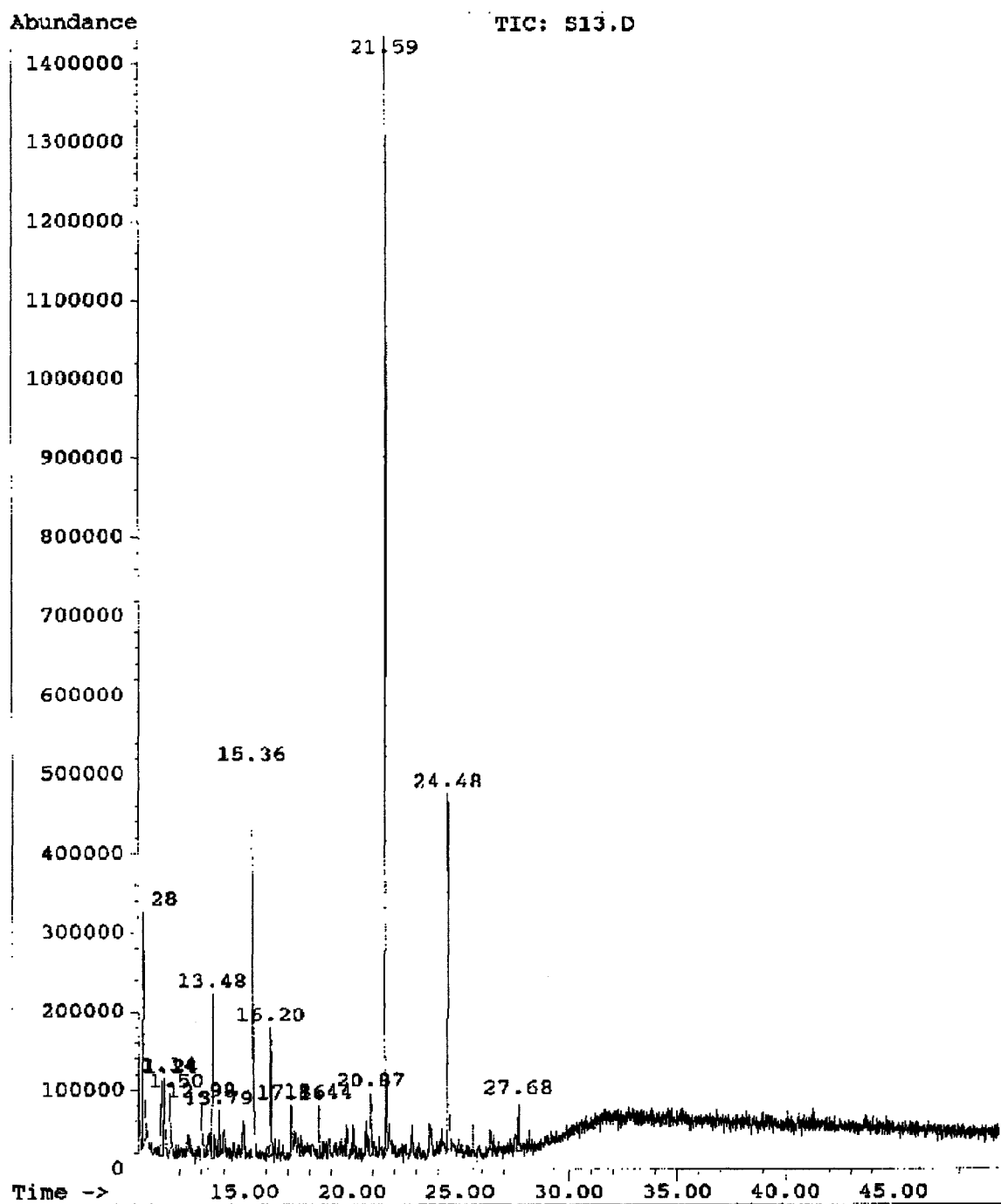


Figure 9 – Chromatogram of the unknown sample S<sub>13</sub>.

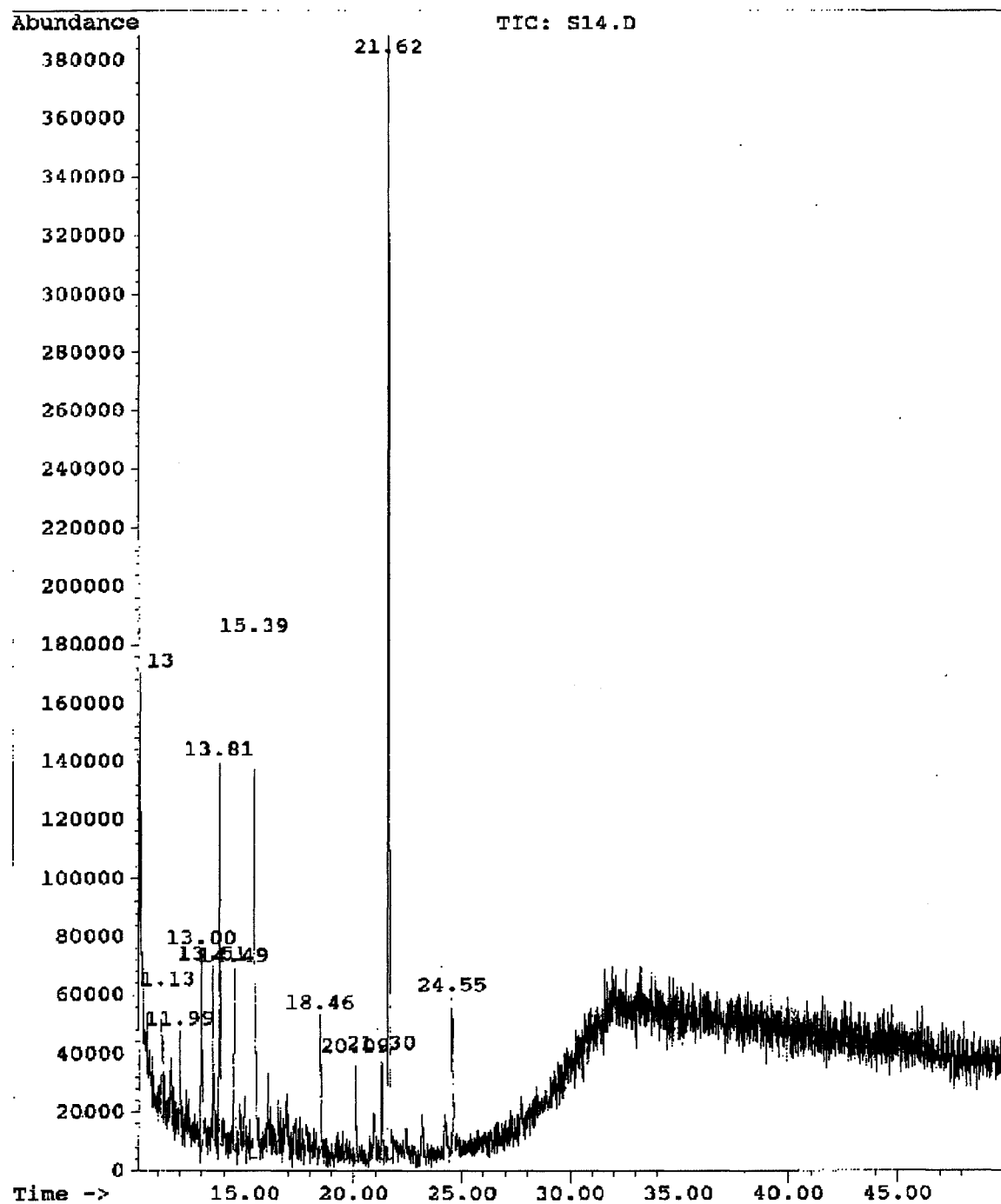


Figure 10 – Chromatogram of the unknown sample S<sub>14</sub>.

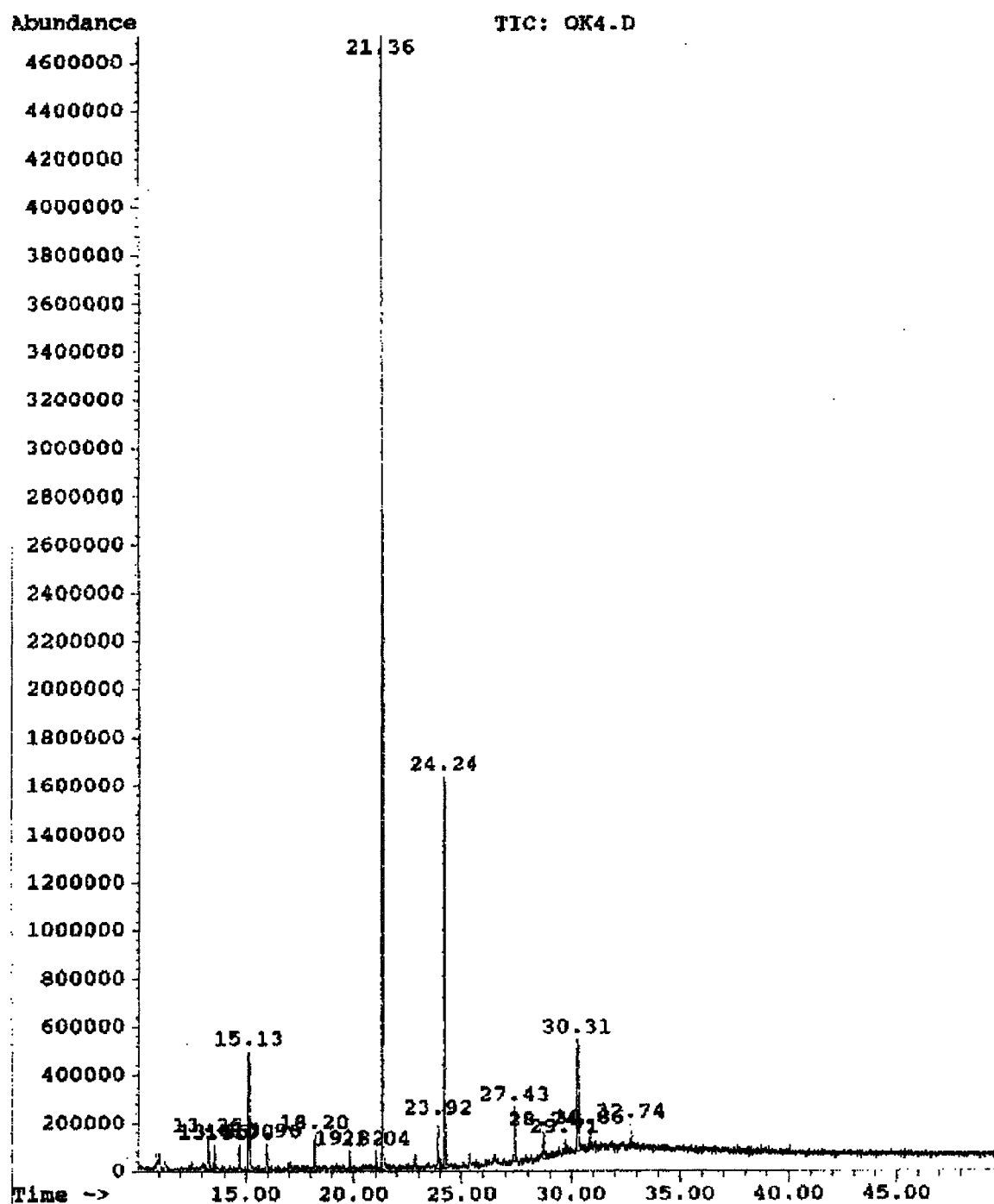


Figure 11 – Chromatogram of the unknown sample S<sub>19</sub>.

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